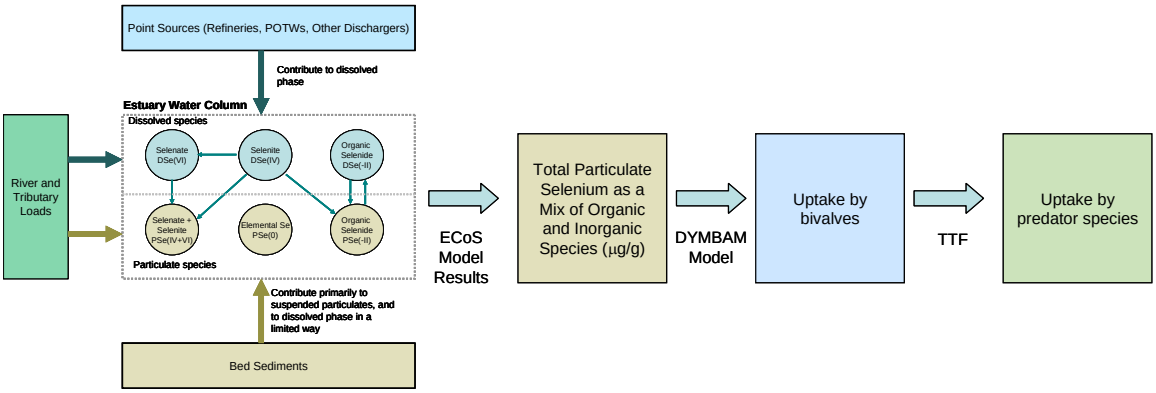
TECHNICAL MEMORANDUM 6: APPLICATION OF ECOS3 FOR SIMULATION OF SELENIUM FATE AND TRANSPORT IN NORTH SAN FRANCISCO BAY

Final Report, February 2010



Prepared for:
Regional Water Quality Control Board
San Francisco Bay Region
1515 Clay Street
Oakland, CA 94612

Prepared by:
Tetra Tech, Inc.
3746 Mt. Diablo Blvd., Suite 300
Lafayette, CA 94549

This Technical Memorandum has undergone a scientific review by the Technical Review Committee, and we thank the reviewers for their contribution to the preparation of this report.

Technical Review Committee members:

- Dr. Nicholas S. Fisher, State University of New York, Stony Brook
- Dr. Regina G. Linville, California State Office of Environmental Health Hazard Assessment
- Dr. Samuel N. Luoma, Emeritus, U.S. Geological Survey
- Dr. John J. Oram, San Francisco Estuary Institute

The role of the Technical Review Committee was to provide expert reviews of the modeling process as well as credible technical advice on specific issues arising from the review process. Appendix 5 provides a record of the technical review process, presents the comments of the Technical Review Committee members, and identifies the actions that were taken in response to the Technical Review Committee's comments.

We would like to thank Shannon Meseck (National Marine Fisheries Service) and Gregory Cutter (Old Dominion University) for providing the code for an earlier version of the model and for providing selenium data in San Francisco Bay. We would also like to thank John Harris (formerly of the Plymouth Marine Laboratory, United Kingdom) for providing a copy of the ECoS modeling framework for use in this work.

ABBREVIATIONS

AE	Assimilation Efficiency
BDAT	Bay Delta and Tributaries
BEPS	Bed Exchangeable Particles
CIMIS	California Irrigation Management Information System
DYMBAM	Dynamic Multi-Pathway Bioaccumulation Model
ECoS	Estuarine Contaminant Simulator
ETM	Estuarine Turbidity Maximum
IEP	Interagency Ecological Program
IR	Ingestion Rate
RMP	Regional Monitoring Program (in the San Francisco Bay)
NDOI	Net Delta Outflow Index
NSFB	North San Francisco Bay
POTW	Publicly Owned Treatment Works
PSP	Permanently Suspended Particles
SFEI	San Francisco Estuary Institute
TMDL	Total Maximum Daily Load
TTF	Trophic Transfer Factor
TSM	Total Suspended Material
USGS	United States Geological Survey

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EXECUTIVE SUMMARY

This document describes the development and application of a numerical model of selenium fate and transport in the North San Francisco Bay (NSFB), in support of the development of a selenium TMDL in this water body. The numerical model formulation is based on the conceptual model of selenium in NSFB that was reported earlier (Tetra Tech, 2008c). The conceptual model described the point and non-point sources of selenium to the bay and transformation and biological uptake processes in the bay. The flows and selenium loads from the Sacramento and San Joaquin Rivers are dominant in the bay, although in the dry season, some of the point sources, such as refineries, can become more important. Dissolved selenium concentrations in the NSFB are low. However, selenium present in particulate forms in the water column of the estuary bioaccumulates in filter feeders, such as bivalves, and then into predator organisms that feed on these bivalves. Selenium-associated impairment in NSFB is largely a consequence of high concentrations in these predator organisms, specifically the white sturgeon and diving ducks.

An estuary model (developed using the ECoS 3 framework) was used to simulate the selenium concentrations in the water column and bioaccumulation of selenium in the NSFB. The model built upon the previous work of Meseck and Cutter (2006). The model was applied in one-dimensional form to simulate several constituents including salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium and selenium concentrations in bivalves and higher trophic organisms. The biogeochemistry of selenium, including transformations among different species of dissolved and particulate selenium and bioaccumulation through foodweb were simulated by the model.

Selenium species simulated by the model include selenite, selenate, and organic selenide. The particulate species simulated by the model include particulate organic selenium, particulate elemental selenium, and particulate adsorbed selenite and selenate. The uptake of dissolved selenium by phytoplankton includes uptake of three species (selenite, organic selenide and selenate). Bioaccumulation of particulate selenium to the bivalves was simulated using a dynamic bioaccumulation model (DYMBAM, Presser and Luoma, 2006), applied in a steady state mode. Bioaccumulation into bivalves considers the different efficiencies of absorption for different selenium species. Bioaccumulation to higher trophic levels of fish and diving ducks is simulated using previously derived linear regression equations by Presser and Luoma (2006), and using estimates of trophic transfer factors summarized from the literature (Presser and Luoma, personal communication, 2009). Trophic transfer factors (TTFs) are the ratio between dietary concentrations and tissue concentrations in predator organisms, and have been found to vary over a surprisingly narrow range across species and habitats. The TTFs are a relatively simple and elegant way to incorporate biological uptake from bivalves to predator species in this model.

The modeling as presented here consists of calibration and evaluation prior to its use in a predictive mode. The calibration process involves the adjustment of model parameter values to obtain the best possible fit to the measured data for selected water quality constituents that are related to selenium fate and transport. Once the parameter values have been defined through calibration, the evaluation process consists of applying the model to different time periods to compare outputs against measurements. Evaluation for time periods outside the

calibration period provides more confidence in model's ability to predict conditions that fall outside of the calibration period. The model was calibrated using salinity, TSM and phytoplankton data obtained from the USGS for 1999 and evaluated using data from 2000 through 2007. The selenium concentrations used in the model calibration were data from Cutter and Cutter (2004) and Doblin et al. (2006), which contain detailed selenium speciation information for April and November 1999. The model was evaluated using selenium data from the RMP for 2000-2005. The model performed well under different hydrological and load conditions, and was able to simulate salinity profiles and long-term patterns in TSM and chlorophyll a concentrations relatively well.

The calibrated model was also run in a hindcast mode using hydrological conditions and selenium loads for 1986 and 1998. Selenium species and loads in these periods were different from current loads, and the hindcast is another test of the credibility of the model. The simulated dissolved selenium concentrations compared well to the observed data. The model was able to simulate the mid-estuarine peaks in selenite for low flow of 1986 and 1998. This indicates that the location and magnitude of the selenium input from point sources and the transport and transformation of selenium are represented well in the model. Simulated particulate selenium concentrations also compared well with the observed values.

Although the calibration process was extensive, and generally described key constituents of interest across a range of years, seasons, and loading conditions, using a relatively small number of adjustable parameters, several features could not be fully captured by the model. This includes peaks in concentrations for constituents such as TSM and phytoplankton, represented by chlorophyll a concentrations. This is likely attributable to the limitations of the one-dimensional model in capturing the complexities of processes in the NSFB, and also to seasonal changes that were not fully parameterized during calibration. Although the model as presented here contains a great deal of the mechanistic detail associated with selenium transformations and biological uptake, it must be recognized that any one-dimensional model will have limitations in representing the full range of processes occurring in the NSFB.

Several hypothetical load reduction scenarios were presented to illustrate the relationship between sources and endpoint concentrations (dissolved, particulate, and bivalve concentrations). These load reductions are not proposed TMDL allocations but were meant to provide further insight into the estuary behavior as embodied in this model.

All scenarios consider that the Sacramento River dissolved concentrations are at a regional background level (about 0.07 µg/l), and that dissolved loads from this source are not modified. With the Sacramento River dissolved concentrations used to establish baseline conditions, changes were made to dissolved selenium loads from refineries, POTWs and other point sources, local tributaries, and the San Joaquin River. Concentrations were changed separately for the particulate load originating from the Sacramento and San Joaquin Rivers.

Particulate selenium concentrations in the flows from Sacramento River were provided as a range, reflecting the uncertainty in this input. The only available data are from Rio Vista which is tidally influenced and therefore may not represent the concentrations from the

Sacramento River. For suspended particulates the range in concentrations was 0.46 to 0.75 µg/g, and for bed exchangeable particulates, the range was 0.25 to 0.5 µg/g. Phytoplankton selenium concentrations were expressed as a Se:C ratio, and set at 15.9 µg/g at the riverine boundary. The range of boundary conditions used for Rio Vista may be high for what is considered to be a relatively uncontaminated river, but the use of values lower than this would not be consistent with observed concentrations of selenium in particulates in the bay.

Although the dissolved and particulate loads were treated separately for the purpose of the load scenarios, once in the estuary, the forms are interrelated through the equations for uptake, mineralization, and adsorption/desorption. However, these transformations are rate limited, with literature or calibrated values of rate constants. Given the residence times in the estuary, the uptake rates provide a limit to how fast forms of selenium can change from dissolved to particulate and vice versa.

When dissolved loads, including point sources and local tributary contributions, are reduced, there are corresponding decreases in the dissolved concentrations, but minimal change in particulate species concentrations. The exception is for a tripling of the San Joaquin River dissolved load: this has a major impact on dissolved phase concentrations, and a smaller, although still significant, impact on the particulate concentrations. In comparison, a decrease of the San Joaquin River dissolved load shows limited impact on dissolved and particulate concentrations, in large part because the decrease is inundated by the contribution of the Sacramento River dissolved load. A modification of the scenario with the tripling of the San Joaquin River dissolved load (imposed by changing the concentration, but holding the flow the same as the base case) was performed by allowing delivery of Vernalis-level flows directly to the delta, with no attenuation due to aqueduct withdrawals. This resulted in a similar increase in dissolved and particulate selenium concentrations in NSFB.

A tripling and a halving of the Sacramento River particulate load only (the dissolved load was unchanged), showed a major effect on the particulate and bivalve selenium concentrations (an increase and a decrease respectively). This highlights the critical role played by this input, and the need for it to be characterized accurately. This load is different from the other loads in that it is not likely to be modified through specific actions; however, given its importance, it is poorly characterized over the period of the simulation.

The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year, i.e., for a given load change factor, greater change is observed during the dry periods. This relates to the lower contribution from the Sacramento River during these periods and the longer residence times in the bay. This highlights the need for focusing on dry periods during which the impacts to the bay may be more easily observed.

The scenarios presented provide insight into the representation of the bay in the ECoS model framework, and allow evaluation of the underlying model formulation presented here. They demonstrate the somewhat different behavior of dissolved and particulate selenium over time scales and residence times that pertain to the simulation period, even though it is known that the two phases are inter-related through uptake, mineralization, and adsorption/desorption. In this regard, the model formulation is distinct from the Presser and

Luoma (2006) formulation that relates dissolved phase concentrations to particulate concentrations through equilibrium-type partitioning, with dissolved concentrations changes causing proportional changes in particulate concentrations.

The scenario calculations indicated that reducing local selenium inputs from refineries, POTWs and tributaries will result in decreases in the dissolved selenium concentrations. The decreases were not proportional to the load reductions, however, because the Sacramento River load remained constant. Importantly, changes in particulate concentrations of selenium (expressed as μg/g) are much smaller than dissolved concentration changes. For several load scenarios considered where loads were decreased, the particulate concentration changes in the bay were small. This is primarily a consequence of the existence of the baseline-level particulate concentrations that are established by the dominant Sacramento River inflows. As conceptualized in this work, and elsewhere, the uptake of particulate selenium by bivalves is a critical step in the bioaccumulation of selenium in predator organisms. The finding that during the high flow season, particulate concentrations in the bay are relatively insensitive to decreases in dissolved selenium loads is significant from the standpoint of the TMDL.

Importantly, however, the model showed that particulate load increases from the San Joaquin River could result in higher particulate concentrations (expressed as μg/g) with consequent impacts on bivalves and organisms that feed on them. When particulate loads from the San Joaquin River are lowered, particulate selenium concentrations in the Sacramento River set the lower-bound concentrations for the bay.

The combination of data and model outputs presented in this memorandum can be used to make a strong case for using this modeling approach in the development of the NSFB selenium TMDL. Although there remain areas where better fits between observations and model outputs are desirable, the limiting factor may be the use of a one-dimensional model and the absence of data to develop a more spatially and temporally resolved model. Given the present-day availability of data, the model presented here is considered suitable for conducting analyses relating selenium sources to concentrations in various biotic and abiotic compartments. The model can also be used to explore the transformations of selenium, and the fluxes between different compartments, to more fully understand the processes that result in elevated selenium concentrations found in higher-trophic level organisms in the bay.

Besides developing load allocations, the model can be used to devise monitoring strategies for different compartments and implementation strategies for attaining TMDL objectives. The model can also be used to explore system responses when conditions are very different from current conditions, with higher phytoplankton concentrations, or more extreme dry periods, for example. However, the model does not represent selenium uptake mechanistically beyond the level of the bivalves, and thus bioaccumulation into predator species is represented using previously developed regression equations (Presser and Luoma, 2006). The trophic transfer factors (TTF), which are based on kinetic uptake parameters, provide a better approach to link selenium concentrations in diets and fish tissues. The results using trophic transfer factors to link selenium concentrations in bivalves and white sturgeon tissues are also presented. Furthermore, transport to specific target organs, such as

the liver or ovaries, in species of interest, is also not considered mechanistically in this work. Controlled feeding experiments with predator species such as the white sturgeon have been reported (Linville, 2006), and depending on the nature of the target chosen for the selenium TMDL, mechanistic representation of bioaccumulation in such species may be considered in future modeling.

Overall, the modeling performed to date and the published field data incorporated in this effort, lends support to the following general conclusions of relevance to the TMDL:

- The major riverine inflows to the NSFB (Sacramento and San Joaquin) form the main loads of dissolved selenium. However, dissolved concentrations in the Sacramento River are a tenth of those in San Joaquin River (~0.07 µg/l compared to ~0.7 µg/l). Sacramento River flows are typically several times larger, and the dissolved load contributions from both sources to the Delta are of similar magnitude.
- The pathway of most concern from the standpoint of selenium bioaccumulation is the transfer of selenium from particulates to bivalves and the predator species that consume these bivalves.
- The selenium form of most concern in the bay is particulate selenium, which is largely supplied by the riverine loads. Selenium in the water column in the dissolved form may be converted to particulate forms, through phytoplankton uptake and adsorption, but the transformations are highly species specific: selenate interacts minimally with particles, whereas both selenite and organic selenide are more reactive. Should future efforts be focused on the derivation of a partitioning coefficient, or K_d, for selenium, the emphasis must be on deriving species-specific values. If a net K_d is estimated, representing all species of selenium, the value is highly variable depending on the season and flow conditions driven by changing selenium species in the bay.
- The bioaccumulation analysis presents a focused and possibly incomplete evaluation of the adverse effects of selenium uptake on fish and bird species that are benthic feeders. The bivalves chosen for examination in this work, *Corbula amurensis*, are very efficient at bioaccumulating selenium, more so than other bivalve species. In the bioaccumulation analysis, it is assumed that the predator species, white sturgeon and diving ducks, feed exclusively on this bivalve species. The risks to predator species in the bay from selenium uptake are very sensitive to change in the particulate concentrations because of the presence of *Corbula amurensis*, an organism that bioaccumulates Se strongly when small changes in particulate concentrations occur and pass that selenium up the benthic food web.
- From the standpoint of managing the selenium impacts to the identified biota in the bay, the most effective option is to control the particulate sources. Data from mid 1980s and late 1990s, although limited, show that dissolved and particulate concentrations do not have a simple proportional relationship in the estuary: large reductions in point source loads decreased dissolved phase concentrations, but had a small impact on particulate concentrations. The relationship between dissolved and particulate selenium concentrations in the bay is complex, and more focused data

collection and/or laboratory studies need to be performed to better characterize the transformations between different forms of selenium

- The modeling also shows that while decreases in particulate concentration (in µg/g) may be difficult to achieve, increases in concentration are possible, should there be increased loads from the San Joaquin basin by means of higher flows into the Delta. Given the range of modifications that are being proposed for the Delta waterways to improve water supplies for export, the likelihood of increased concentrations should be actively considered in the TMDL process.

The analysis presented in this work leads to the following recommendations:

- There is a need for more detailed data collection and an ongoing selenium research program in the San Francisco Bay estuary. The work presented here in some aspects relies on selenium data collected nearly a decade ago. Given the importance of selenium in the bay ecosystem, and knowledge of the pathways of bioaccumulation, a focused monitoring and research program, updated on a periodic basis, will greatly benefit selenium management in the region.
- The model simulations show that the selected particulate selenium concentrations at the system boundaries (Delta and Golden Gate Bridge) have a significant effect on the predicted particulate selenium concentrations in the water column and the bioaccumulation of selenium by clams. The modeling results are based on the use of existing data to characterize the boundary conditions. The lack of particulate selenium concentration measurements on the Sacramento River at Freeport and in the near-shore area beyond the Golden Gate Bridge is a prominent deficiency. The accurate characterization of the particulate concentrations at the boundaries of the system through field sampling efforts is essential.
- A great deal of ongoing monitoring in the bay, Delta, San Joaquin River, and aqueducts is in terms of total selenium. This study shows the limited utility of these data in characterizing bioaccumulation and ecological risk. At a minimum, such monitoring should include measurement of dissolved and particulate selenium. Monitoring must be performed using the lowest detection limits possible; much of the current routine monitoring in the Delta and aqueducts, performed with a detection limit of 0.5 µg/l, shows large numbers of samples with non-detectable concentrations.
- Given the importance of the bioaccumulation of selenium and the transfer to higher organisms by *Corbula amurensis,* additional field and laboratory investigations to characterize its distribution, feeding behavior, and selenium assimilation under varying forms of selenium and particle sizes would significantly contribute the reduction in uncertainty.
- The modeling approach is able to capture the key features of selenium behavior in the system at a level that is consistent with data that can be measured. This model as currently set up can be used to explore management options in the context of the TMDL. Analysis of new speciation data with the model will be very useful.

Future model development may seek to address some of the shortcomings of the modeling presented here, such as an inability to capture the full temporal variability of ancillary parameters such as TSM and chlorophyll, the uncertainties in riverine and ocean boundary conditions and their effect on the conclusions, and the inability to reproduce the large local-scale variability in organic selenium concentrations, but such model development must be preceded by an adequate data collection program.

1. INTRODUCTION

The San Francisco Bay Regional Board is developing a selenium Total Maximum Daily Load (TMDL) for North San Francisco Bay (NSFB), due to high concentrations in some organisms. Towards that end, the Regional Board needs to conduct analyses that help explain the linkage between selenium inflows into the system and concentrations in biota of concern. In support of this effort since mid-2007, Tetra Tech has prepared a series of Technical Memorandums (TMs) focusing on individual topics of relevance to the TMDL. These TMs have included a summary of the loads of selenium to the NSFB (TM-2), a review of the selenium toxicology literature (TM-3), a conceptual model of selenium in the system (TM-4), and an overview of possible modeling approaches (TM-5) (Tetra Tech, 2008 a,b,c,d). This document (TM-6) presents the development and an application of a numerical model of selenium fate and transport in NSFB.

TMs 2-5 set the stage for the modeling presented here; this information is summarized briefly in this section, and interested readers are referred to the original documents for more detailed background information.

There has been a long history of research on selenium sources, transport, and biological uptake in San Francisco Bay, the Delta, and in the Central Valley which these series of support documents build upon (e.g., White et al., 1987, 1988, 1989; Cutter, 1989; Cutter and San Diego-McGlone, 1990; Cutter and Cutter, 2004; Presser and Luoma, 2006; Meseck and Cutter, 2006). Starting in the mid-1980's, selenium concentrations have been monitored in the bay across the salinity gradient and in different seasons reflecting variations in freshwater flows. Major sources of selenium to the Bay-Delta include:

- San Joaquin River that receives discharge from agricultural drainage from the western San Joaquin Valley
- Selenium discharged from the effluents of North Bay refineries.
- Sacramento River, which is the dominant freshwater inflow to the Bay-Delta during the wet season.
- Local tributaries (i.e., besides discharges through the Delta, largely represented by the Sacramento and San Joaquin Rivers) that discharge directly into NSFB. This may include background loads, as well as non-point loads representative of the urban and agricultural land use in their watersheds.
- Publicly owned treatment works and other NPDES dischargers that discharge directly into the bay or into tributaries near the bay.

Using flow and concentration data from each of the sources, the detailed source analysis quantified the relative magnitudes as well as the seasonal and inter-annual variability in these loads (Tetra Tech, 2008a). The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas are also a large source of selenium (estimated average load of 354-834 kg/yr). Refineries are now estimated to be the third largest source of selenium to the North Bay (538 kg/yr), although these loads were about three times higher prior to mid-1998 when wastewater controls were installed. Sediment resuspension/erosion and diffusion (293 kg/yr), other wastewater discharges (250 kg/yr),

and atmospheric deposition (18-164 kg/yr) are other, smaller contributors to the total selenium load. The rivers are also a major contributor of the particulate selenium load, a component that is of great significance in the uptake of selenium by bivalves and subsequently by fish.

The conceptual model presented an overview of the current understanding of selenium biogeochemistry and uptake by organisms in NSFB. Selenium behavior in three principal compartments was described, including the water column, sediments, both suspended and bedded, and biota (Tetra Tech, 2008c). This background information is summarized here.

- **Water Column:** Selenium enters NSFB in dissolved and particulate forms from the Delta, from point sources such as the refineries and municipal wastewater treatment plants, and from local tributaries. The primary sources of selenium in the suspended sediment form are the non-point sources. Phytoplankton production and sediment bed erosion are also sources. Both dissolved and particulate selenium can exist as different species that affect their cycling and bioavailability (selenate, selenite, organic selenides, and elemental selenium). Dissolved selenium can be taken up and bioconcentrated by algae and bacteria in the water column and add to the supply of particulate selenium. Selenite is the most bioavailable and bioaccumulative form of dissolved selenium. The exchange between selenate and selenite is slow, and is unlikely to occur significantly over the residence times in the bay. Conversion of selenite to organic selenide forms through microbial uptake is more rapid and is likely to be important in the bay.
- **Sediments:** Depending on the flow rate and season, deposition to and erosion from the sediment bed can also be a sink/source of particulate selenium to the water column. Sediments are more reducing than the water column, and may result in conditions that reduce selenate and selenite to elemental selenium, Se (0), a form that is insoluble and less bioaccumulative than selenite.
- **Biota:** Because of the partitioning of some forms of selenium onto particles, and the active uptake by algae, particulates in NSFB (comprising of mineral and organic particles, and live and senescing algae) are a comparatively rich source of selenium to organisms that consume them. Filter-feeding benthic organisms such as bivalves ingest and assimilate the particulate forms of selenium at different efficiencies depending on the type of particulate material. Direct absorption of dissolved selenium is minimal for organisms besides phytoplankton and bacteria. Bivalves, particularly *Corbula amurensis*, typically biomagnify selenium to concentrations higher than found in the particulate phase. When these organisms are consumed by predator species such as white sturgeon and diving ducks, the selenium is biomagnified further in the tissues of these animals. Algal and bacterial-associated selenium can also enter the food through a non-benthic pathway, i.e., through zooplankton that feed on these organisms, and through consumer organisms that feed on zooplankton. However, selenium concentrations in the non-benthic pathway foodwebs are closer to non-contaminated background concentrations.

The external source characterization, and the internal transformations of selenium set the stage for the numerical modeling presented in this document. An estuary modeling

framework ECoS 3 (v 3.39) (Gorley and Harris, 1998) was used as the basis to simulate the transport and dynamics of selenium and bioaccumulation through key elements of the food-web in the NSFB. The ultimate goal of the modeling is to relate point and non-point selenium loads to endpoint concentrations of concern, in this case concentrations in biota. ECoS 3 is a modeling framework developed by the Center of Coastal and Marine Sciences at the Plymouth Marine Laboratory, U.K. (Harris and Gorley, 1998). This modeling framework was previously applied to the NSFB to simulate the biogeochemistry of selenium by Meseck and Cutter (2006). The work presented here extends the previous work of Meseck and Cutter (2006) for the TMDL application.

Physical and geochemical processes have been studied through modeling in the San Francisco Bay over the last two decades, including hydrodynamics and salinity (Casulli and Cheng, 1992; Cheng et al., 1993; Uncles and Peterson, 1995; Gross et al., 1999; Cheng and Casulli, 2001), real-time modeling of the movement of spilled contaminants in the bay through tidal action (NOWCAST system, Cheng and Smith, 1998), suspended sediments (McDonald and Cheng, 1997), and fate and transport of PCBs (Oram et al., 2008). Besides these, two recently published models of selenium in the San Francisco Bay have also been developed (Presser and Luoma, 2006; and Meseck and Cutter, 2006).

The ECoS 3 modeling framework, and the NSFB-specific model as developed by Meseck and Cutter (2006), was selected for this modeling effort because it can be used to represent transport and biotic and abiotic selenium reactions. The model has been calibrated and evaluated using data in the NSFB. The original model has been peer reviewed and the associated computer code made available to us by the original authors. However, the model does not include bioaccumulation processes which are expected to be important for the selenium TMDL. The biological components of selenium uptake are based on the Presser and Luoma (2006) approach, which considers the uptake of selenium from the water column to bivalves, and includes uptake to higher trophic levels using trophic transfer factors between diet and predator tissue based on a review of the literature (Presser and Luoma, personal communication, 2009). TM-5 (Tetra Tech, 2008) provides more details on the model selection processes.

To model selenium in the NSFB, ancillary water quality constituents also need to be considered. Constituents simulated by the model include: salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium, and bioaccumulation of selenium through the food-web (Figure 1-1). Salinity serves as a conservative tracer of dissolved solutes in the estuary. Dynamics of TSM reflect the transport of particulate selenium. A key process transforming selenium from the dissolved forms to the particulate forms is through phytoplankton uptake (Baines et al. 2001); therefore, simulation of dynamics of phytoplankton is also important. An important focus of the TMDL is the high selenium concentrations in water fowl and certain species of fish that feed on the benthos. Components that link particulate selenium concentrations to bivalves and predator organisms (white sturgeon and diving ducks) are included in the model. The location of NSFB and the starting point of modeling domain (the "head" of the estuary) are shown in Figure 1-2. The end of the modeling domain is at Golden Gate Bridge. For this application, the NSFB is modeled as a one dimensional, vertically well-mixed, estuary with 33 segments. The approximate locations of the 33 segments are shown in Figure 1-3.

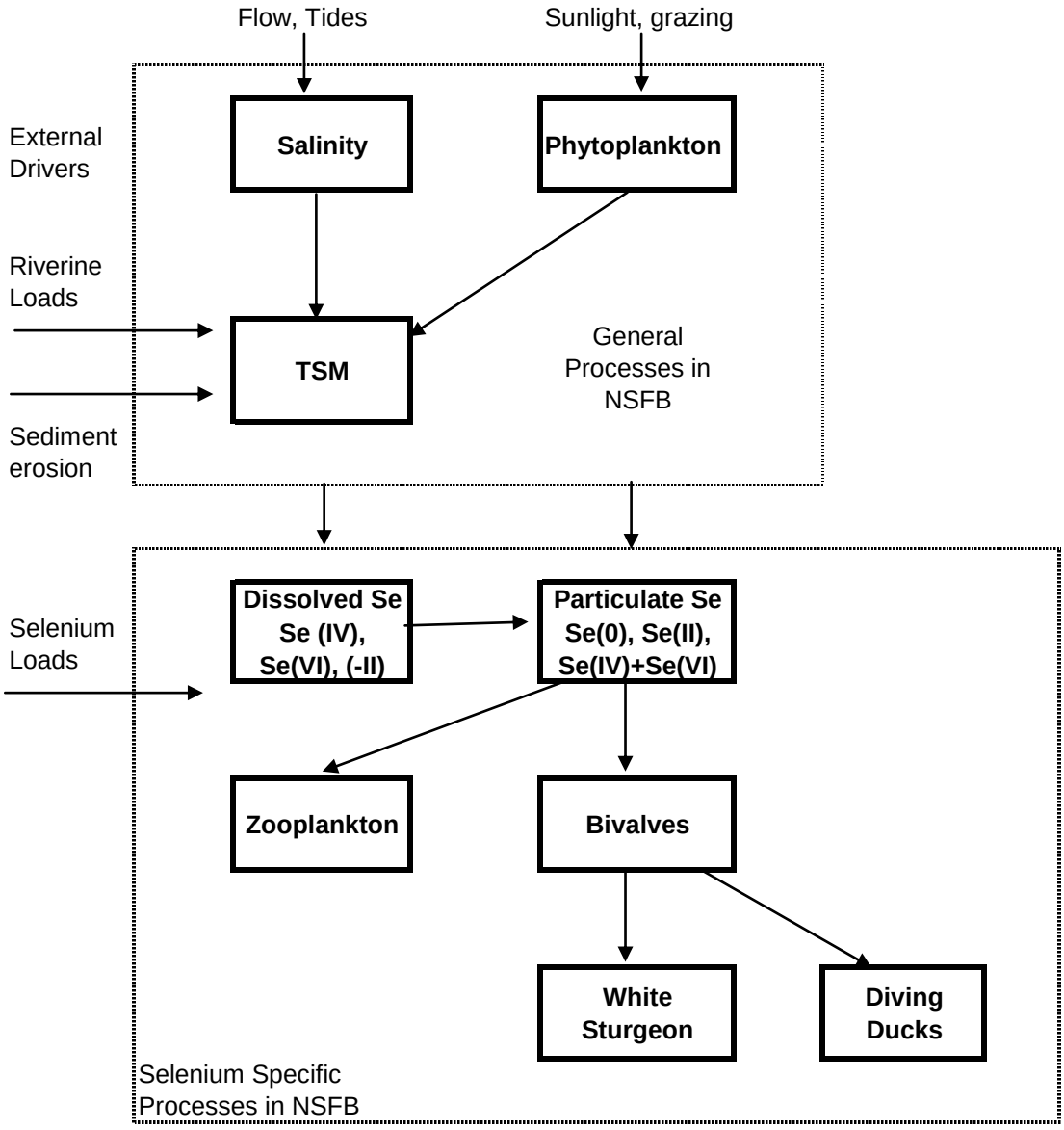


Figure 1-1 Components modeled in the ECoS3 application in NSFB.

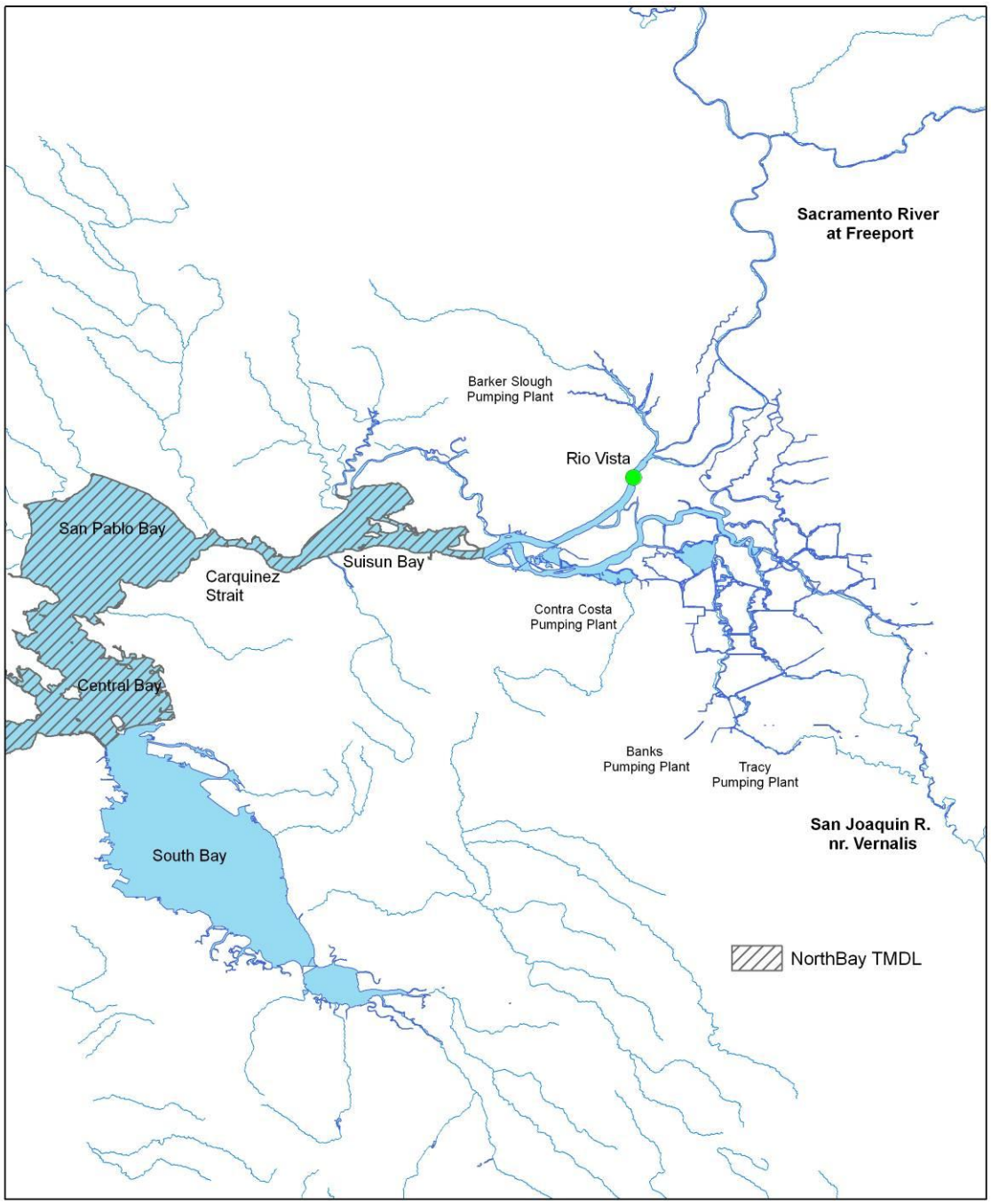


Figure 1-2 **San Francisco Bay and surroundings. The model uses Rio Vista on Sacramento River as the starting point of the simulations, following Meseck and Cutter (2006). San Joaquin River inflows are added as a tributary 19 km downstream of Rio Vista. The Delta is not explicitly modeled in this application.**

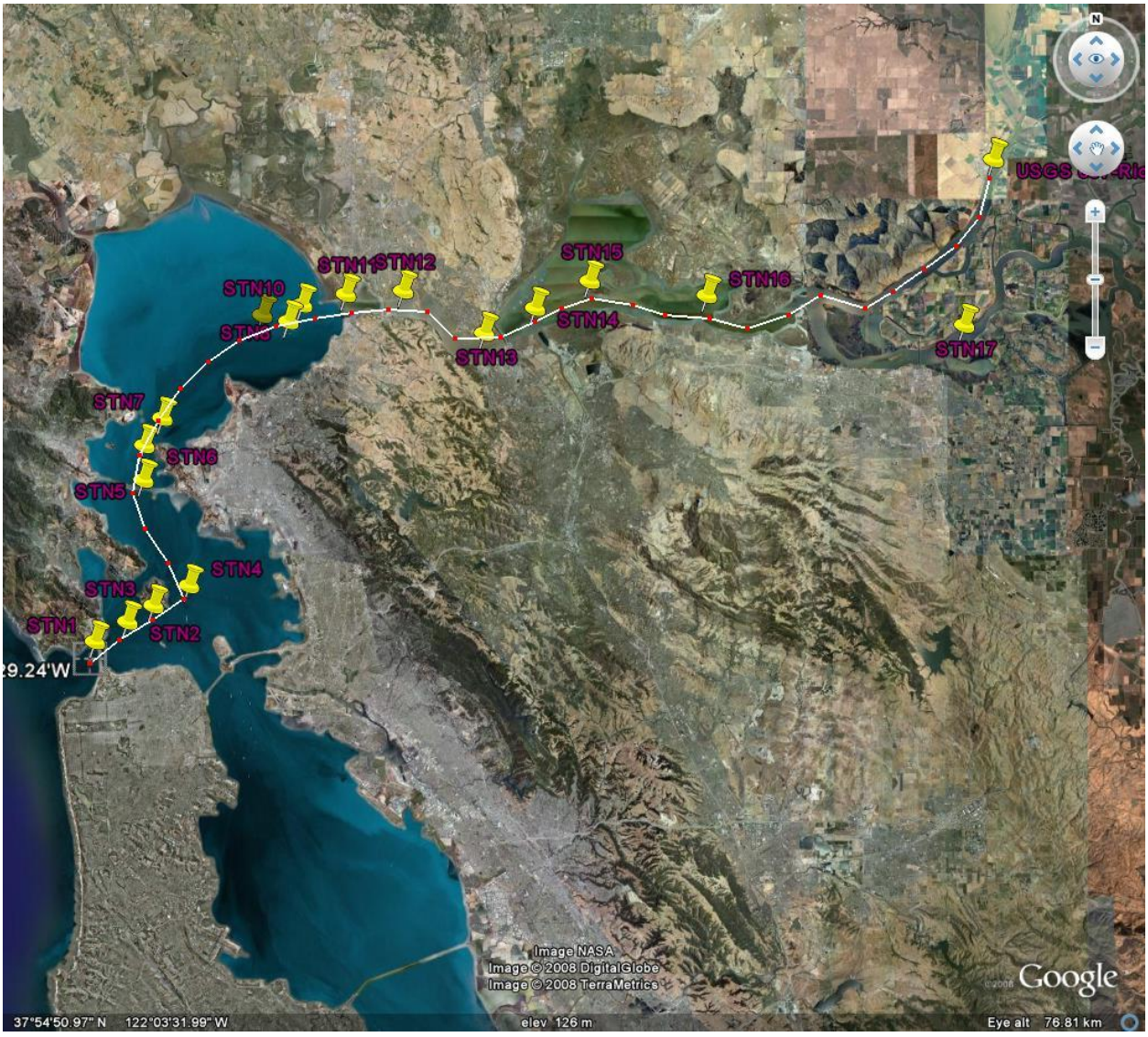


Figure 1-3 Approximate locations for 33 modeling segments in the NSFB (red dots). Yellow pins represent sampling locations in Cutter and Cutter (2004).

The purpose of the model application is to address several issues that are pertinent to the TMDL including:

1. The linkages between selenium sources and endpoints of impairment, including selenium concentrations in water column and biota.
2. Transformations between different species of selenium, and the response of particulate selenium concentrations in the bay to changes in riverine and point source loads.
3. The most effective ways of controlling selenium sources to achieve lower concentrations in particulate forms, and therefore in clams.
4. The contribution of the San Joaquin River selenium loads to the bay, and the consequences of changing this load on concentrations in biota.

5. The role of phytoplankton uptake in converting dissolved selenium to particulate selenium.

Insights developed from the modeling framework will be used to address these key issues in this document.

Modifications made to the original model of Meseck and Cutter (2006) for application in this regulatory setting can be grouped in the following general areas.

- Refinery loads: Daily selenium inputs from five refineries in the NSFB estimated based on daily flow and weekly concentrations for the period of 1999-2007 were added to model cells based on their discharge locations.
- Tributary loads: Selenium loads from local tributaries were added to the model based on their discharge locations. These loads were not identified in the prior application and may be significant in wet months.
- Publicly Owned Treatment Works (POTW) and other point source loads: Loads from POTWs and other NPDES point source dischargers in the NSFB were added to the model. Loads from these sources are smaller than other sources identified (TM-2, Tetra Tech, 2008), however they are related to the TMDL process because it is necessary to account for point source dischargers.
- Inputs of TSM and Phytoplankton from the San Joaquin River: Besides selenium inputs from the San Joaquin River, TSM loads (with TSM concentrations modeled as a function of flow) and phytoplankton loads (with observed phytoplankton concentrations) from the San Joaquin River were also added to the model.
- Sediment water interaction: Transfer between bottom sediment-associated selenium and particle associated selenium was added to the model to represent the exchange of selenium between bottom sediments and water column due to exchange of particles between the two compartments.
- Particulate selenium associated with phytoplankton: The transfer of dissolved selenium to particulate selenium through phytoplankton uptake is an important process in the bioaccumulation of selenium. Therefore particulate selenium associated with phytoplankton uptake was tracked as a separate constituent and was added to the total particulate selenium. Simulated Se:C ratio in phytoplankton was also tracked by the model and was compared to data observed for species found in the bay.
- Seawater endmember selenium concentrations: Particulate selenium concentrations at seawater end member at golden gate observed by Doblin et al. (2006) ranged between 0.8 – 1.0 μg/g, therefore a seawater endmember concentration for each species of particulate selenium was specified.
- Bioaccumulation of selenium through the food-web: A dynamic multi-pathway bioaccumulation model (DYMBAM; Presser and Luoma, 2006) was added to predict tissue selenium concentrations in bivalves; previously developed relationships between prey and predator concentrations by Presser and Luoma (2006) were used to predict bioaccumulation of selenium to the higher trophic levels.

- To better capture the salinity profile along the estuary, based on a recommendation from John Harris, a developer of the ECoS framework, salinity is modeled using a constant dispersion coefficient. This is different from the original application of the model by Meseck and Cutter (2006).

The final version of the application files for the work reported in Meseck and Cutter (2006) was not available for this work. The NSFB application was reconstructed using formulations described in Meseck (2002) and the latest version of the ECoS3 manuals.[1] The reconstructed model was run under the latest available version of ECoS3 (v 3.39). Some changes in model routines have been noted in this version of ECoS3, particularly relating to TSM. The model inputs of flow from the rivers and tributaries (e.g., Napa River) as well as selenium loads were reestablished using the most recent data. The model was extended to run continuously to most current year when flow and selenium load data are available (2006-2007). The TMDL application requires the model framework to take into account selenium loads from different sources at different locations, the reconstructed model used closed riverine boundary conditions with loads instead of concentrations at the riverine boundary. Also different from the original model, each constituent, including the particulate selenium, was now modeled as a separate advecting constituent to facilitate the specification of loads at different locations (e.g., particulate selenium loads from the San Joaquin River). Taken together, the changes above entailed a reconstruction of the model code from the original Meseck and Cutter (2006) application with modifications for the TMDL purposes and updates with the newest data available, as well as a re-calibration to fit the available data.

The modeling as described here consists of calibration and evaluation prior to its use in a predictive mode. The calibration process involves the adjustment of model parameters to obtain the best possible fit to the measured data on selected water quality metrics. Once the parameters have been defined, the evaluation process consists of applying the model to different time periods to compare outputs against measurements. This evaluation process provides credibility of the model's ability to predict conditions that fall outside of the calibration period.

The model calibration and evaluation were based on salinity, TSM and phytoplankton data collected by the U.S. Geological Survey (USGS), and selenium data collected by Dr. Greg Cutter's research group at Old Dominion University (also published in several papers: Cutter, 1989; Cutter and Cutter, 2004; Doblin et al., 2006). The data used in the calibration and evaluation for salinity, TSM and phytoplankton are monthly USGS cruise data. Data from Dr. Cutter's research group are selenium speciation data under high and low flows collected in 5 sampling periods during 1997-1999. Selenium data from the Regional Monitoring Program (RMP) were also used in model evaluation. Locations of USGS monitoring stations, RMP stations, and Cutter and Cutter (2004) sampling stations are shown in Figure 1-4. A summary of data used in model calibration and evaluation is provided in Table 1-1.

[1] An early version of the model code was provided to us by Meseck after the modeling was initiated. This code was used as a reference.

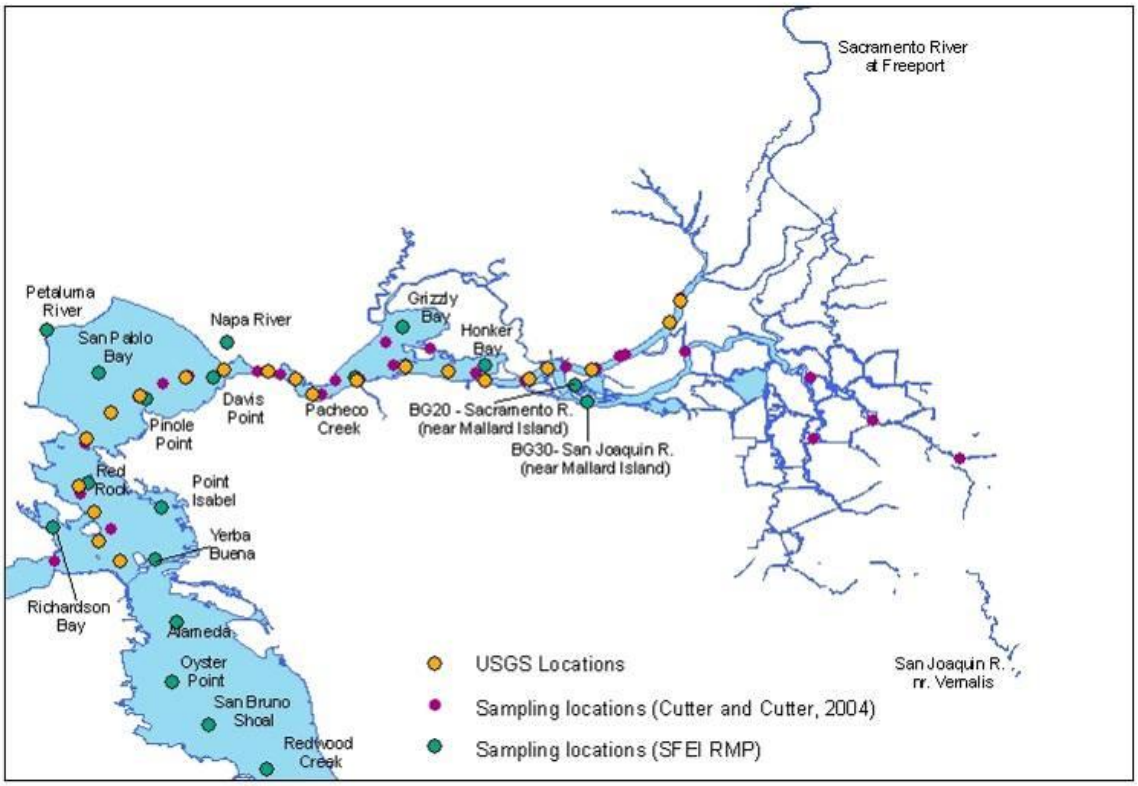


Figure 1-4 **Locations of USGS gaging stations for salinity, chlorophyll a and TSM, SFEI RMP stations and sampling locations by Cutter and Cutter (2004).**

Table 1-1
Data Used in Model Calibration and Evaluation

Data	Description	Source
Salinity, TSM, Phytoplankton	Monthly cruise data at about 21 locations in NSFB	USGS
Selenium Speciation Data	Dissolved and particulate selenium by species along the salinity profile for 5 sampling events during 1997-1999	Cutter and Cutter (2004); Doblin et al., (2006)
Selenium	Dissolved and particulate selenium at an interval of 2-3 sampling events per year from 1993	RMP

The remaining sections of this technical memorandum describe model formulation, calibration and evaluation, and model predictions in the NSFB. Figure 1-5 illustrates the relationship of the different analyses in this document to prior work and the final application of the model in the TMDL process. The following sections are identified in this document and in Figure 1-5.

- Section 2 Modeling Approach-Formulation and Parameterization. This section describes the basic differential equations used to represent processes of interest in selenium fate and transport. It includes representation of salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium and selenium concentrations in biota.

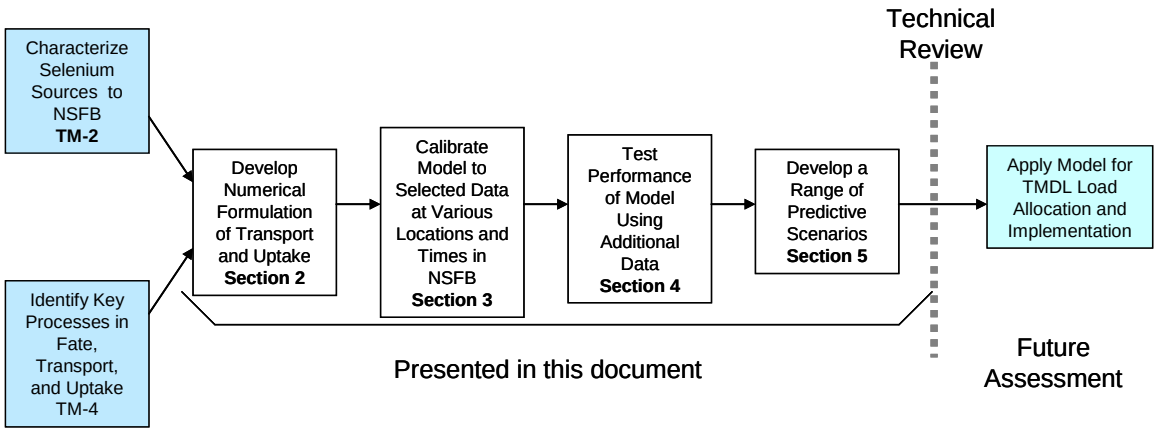


Figure 1-5 Analyses presented in this document related to prior efforts and final application of the model in the TMDL.

- Section 3. Model Calibration and Evaluation. This section describes the application of the model to a set of data from 1999 to estimate the best fit parameters for the equations representing selenium and related water chemistry (calibration). The best-fit parameters are then used to run the model for other time periods, to assess the quality of the fit under conditions different from the calibration condition (evaluation).
- Section 4. Testing Model Performance. The performance of the model is evaluated through a variety of tests, including sensitivity analysis, evaluation of fluxes between different compartments, and mass balance calculations over different time periods. The sensitivity of model outputs to perturbation of the best-fit parameters values is evaluated. Sensitivity analysis identifies parameters that have the most significant impact of model output, and can identify potential areas of weakness in the model prediction. The results of the sensitivity analysis can also help target future data collection. The other tests provide greater insight into the behavior of the model and provide simple checks on the correctness of outputs.
- Section 5. Model Predictions. The calibrated and tested model is used to compute changes in water column and biota concentrations in response to imposed changes in external loads from point and non-point sources. These model runs provide a scientific basis for considering different scenarios to attain targets in the bay.
- Section 6. Discussion. This section contains a discussion of the improved representation of selenium processes embodied in the model and potential limitations, including considerations of limited data availability, and uncertainties arising from the calibration/evaluation process.
- Section 7. Potential Use in the NSFB Selenium TMDL. This section summarizes the proposed role of the model in the TMDL process.

2. MODELING APPROACH – FORMULATION AND PARAMETERIZATION

As previously described in Harris and Gorley (1998), the ECoS3 framework contains modules that simulate transport and dynamics of different dissolved and particulate constituents in an estuary. The framework can be used to simulate dynamics of salinity, suspended sediments, phytoplankton, nutrients and metals (e.g. cadmium; Harris and Gorley, 1998). The ECoS model has been applied to the Humber Estuary of UK for salinity (Harris, 2003), suspended particles, carbon and nitrogen (Tappin et al. 2003), Tweed Estuary of UK for solute transport (Punt et al. 2003) and nutrients (Uncles et al. 2003), and Tamar Estuary for dissolved Zn and Ni (Liu et al. 1998). The ECoS3 software package is a modeling framework that can be applied as 1-D or 2-D form (Harris and Gorley, 2003). The modular structure of the framework allows cut and paste model development. The NSFB application by Meseck and Cutter (2006) is used to simulate different species of selenium.

The dynamics of constituents are generally modeled as a result of advection, dispersion and in-situ transformation:

$$\frac{\partial s}{\partial t} = U\frac{\partial s}{\partial X} - \frac{\partial}{\partial X}(Kx\frac{\partial s}{\partial X}) - \Gamma \quad (1)$$

Where U = velocity, Kx = dispersion coefficient, Γ = in-situ transformation, s = solute concentration and X = length along the estuary. For each time step, the model calculates changes due to *in situ* transformations and then calculates changes due to transport. The initial concentrations and changes in concentrations are used to predict concentrations for the next time step.

Meseck and Cutter (2006) added equations to simulate transport and transformations of different species of selenium in the NSFB. For the Meseck and Cutter application, the NSFB was modeled as a 1-D well-mixed estuary with 33 segments. The model domain starts from freshwater end member at the Sacramento River at Rio Vista (X = 0 m; head) and extends to the mouth at Golden Gate (total length = 101,000 m). The head of the estuary is modeled as a closed boundary with seawater as open boundary. The Meseck and Cutter (2006) spatial representation was used in this work.

Selected data elements, relating to ancillary parameters such as TSM and chlorophyll a, are included in Section 2, where relevant to the model formulation process or to the specification of boundary conditions. Model calibration data are introduced in Section 3.

2.1. SALINITY

The dynamics of salinity along the estuary are a result of mixing of freshwater and seawater, driven by freshwater inflow, wind and tides. During the high flow season, freshwater advection dominates and lower salinity through the estuary is observed. During low flow, salinity in the estuary increases as a result of decreases in freshwater input. Accurate simulation of salinity along the longitudinal transect of the estuary indicates that advection and dispersion of dissolved solutes are simulated correctly. In ECoS3, salinity can be modeled as a result of advection and dispersion (Harris and Gorley, 1998; Meseck, 2002):

$$\frac{\partial S}{\partial t} = -U\frac{\partial S}{\partial x} + Kw\frac{\partial^2 S}{\partial x^2} \quad (2)$$

where U is the water velocity, S is salinity, and Kw is the dispersion coefficient along the axis (X) of the estuary. Freshwater input at the head of the estuary is assumed to have a salinity of 0 and seawater is assumed to have a salinity of 32 psu. The dispersion coefficient is modeled as a single constant which is a calibrated parameter. Water velocity is calculated as flow divided by cross section areas, derived from the Uncles and Peterson (1996) model.

2.2. TRANSPORT OF SEDIMENT

The potential sources of sediments to the bay include the Delta input, local tributaries, *in situ* resuspension and erosion, and *in situ* production due to phytoplankton growth. In ECoS3, two different types of suspended sediment materials are modeled: the permanently suspended particles (PSP) and bed exchangeable particles (BEPS). For the NSFB application, another component of the TSM, phytoplankton, is added to the model. TSM is modeled as the total of PSP, BEPS and phytoplankton biomass:

$$TSM = PSP + BEPS + B \quad (3)$$

where B is phytoplankton biomass (described in the following section 2.3).

The PSP is suspended material that does not sink and does not interact with the bottom sediments, and is modeled in a manner analogous to a dissolved solute (Harris and Gorley, 1998; Meseck, 2002). The dynamics of the PSP is modeled as:

$$\frac{\partial PSP}{\partial t} = -U\frac{\partial PSP}{\partial x} + K_w\frac{\partial PSP}{\partial x^2} + PSP_{river} \quad (4)$$

where PSP_{river} is the riverine input of permanently suspended material (mg/l/d). In ECoS, riverine input of PSP is specified as riverine PSP concentrations, multiplied by flow. Previous studies have found that Sacramento River is the dominant source of suspended sediments to the Bay and discharges seven times more suspended sediments to the Bay the other tributaries including the San Joaquin River (Meseck, 2002). In this application, sediment inputs from the San Joaquin River were also added to the model.

BEPS originates from sediment resuspension. A small portion of the BEPS also originates in the riverine input. Dynamics of BEPS in the estuary reflects sediment-water interaction. BEPS is modeled as a result of sediment resuspension and deposition, as well as advection and dispersion. In the NSFB, an estuarine turbidity maximum (ETM) can form due to tidal asymmetry (Schoellhamer, 2001).

In ECoS3, the tidally averaged sediment transport velocity for BEPS is modeled as:

$$Ubeps = d*(U - e*R*S) \quad (5)$$

where U is the seaward water velocity (m/d), R is the tidal range at mouth (m), and S is salinity. Both d and e are calibration parameters. Parameter d scales the axial velocities in

relation to water velocity and the parameter *e* scales the up-estuary component relative to the seaward transport, and determines the position of the estuary turbidity maximum. Increasing *e* moves the turbidity maximum up-estuary. The value of *d* is usually less than 1 since particle velocity is generally less than water velocity (Harris and Gorley, 1998). Dispersion of BEPS is proportional to mixing due to both freshwater movement and tides.

$$Kbeps = \varepsilon * U + \psi * R * S \quad (6)$$

where ε and ψ are calibration coefficients. Similar formulations were used in simulating transport of suspended particles in the Humber Estuary by Tappin et al. (2003), and a reasonable fit between simulated and observed PSP was found.

Sediment deposition rate is in proportion to BEPS and is modeled as deposition velocity divided by water depth.

$$MD = Vs/H \quad (7)$$

where *Vs* is sediment deposition velocity (m/d) and *H* is water depth (m). Deposition is most significant where the BEPS maximum is found. Sediment deposition velocity was 86.4 m/day based on work by McDonald and Cheng (1997). It was assumed that the total flux of sediments from the estuary bed to the water column is balanced by deposition. Two previous studies from USGS found that NSFB including the San Pablo Bay and Suisun Bay on net is eroding (USGS 2001a, b). The average net erosion rate was estimated to be small, at a value of 0.0063 $kg/m^2/d$. To reflect this effect, sediment resuspension rate is specified as deposition rate plus this net erosion rate.

Little is known regarding the variation in bottom sediment mass across the estuary. Based on a previous literature review, the active sediment depth of the NSFB is assumed to be 15 cm (Leatherbarrow et al. 2005). Similar to Davis (2003), using a sediment density of 2.7 g/m^3 and a solids concentration in sediment of 0.5, the active sediment bed mass is 130.5 kg/m^2.

It was found that spring-neap tidal variations can be significant. Tides are mixed diurnal and semidiurnal and the tidal range varies from about 0.6 m during the weakest neap tides to 1.8 m during the strongest spring tides (Schoellhamer, 2001).

Tidal variation can be simulated using a six component tidal model as in Meseck (2002):

$$TIDE = M_2 + S_2 + K_2 + O_1 + M_4 + M_6 \quad (8)$$

where each component of the tide is defined as:

$$TC(i) = TA(i) * COS((TP(i) - TF(i)*T) * \pi/180) \quad (9)$$

where *TC(i)* is the tidal constituent (e.g. M_2, S_2, K_2), *TA* is tidal amplitude (m), *TP* is tidal phase (degrees), *TF* is the tidal frequency (degrees/day or degrees/hr), π/180 converts the angles of tidal frequency and phase to radians. Main components of tides in Golden Gate are M_2 (0.58m), K_1 (0.37m) and O_1 (0.23m) (Uncles and Peterson, 1996).

2.3. PHYTOPLANKTON

The dynamics of phytoplankton play an important role in regulating selenium transformations. Dissolved selenium can be taken up by phytoplankton to form particulate organic selenium, which is bioavailable to higher trophic level organisms (Luoma et al. 1992). Phytoplankton dynamics in the NSFB are a function of different sources and sinks. Species and concentrations of phytoplankton vary with season and river flow, with lower phytoplankton concentrations coincident with higher river flow (Cloern et al. 1983). Phytoplankton in the estuary is subjected to loss due to respiration, benthic grazing and zooplankton grazing. Benthic grazing can be a controlling factor in phytoplankton biomass (Lucas et al. 2008). Due to the invasion of Asian clam *Corbula amurensis* in NSFB beginning in 1985, dramatic decreases in chlorophyll a concentrations were observed (Alpine and Cloern, 1992). Chlorophyll a concentrations have shown some slight increases in the San Pablo and Central Bays in recent years (Cloern et al. 2006, Figure 2-1).

The NSFB receives high nutrient loadings, and the growth of phytoplankton is considered to be light limited (Cole and Cloern, 1984). Vertical mixing in the NSFB is relatively rapid. Data from USGS monthly cruise sampling suggests relatively uniform chlorophyll a concentrations along the depth profile (Figure 2-2). Therefore, phytoplankton concentrations are assumed to be completely mixed vertically for this effort.

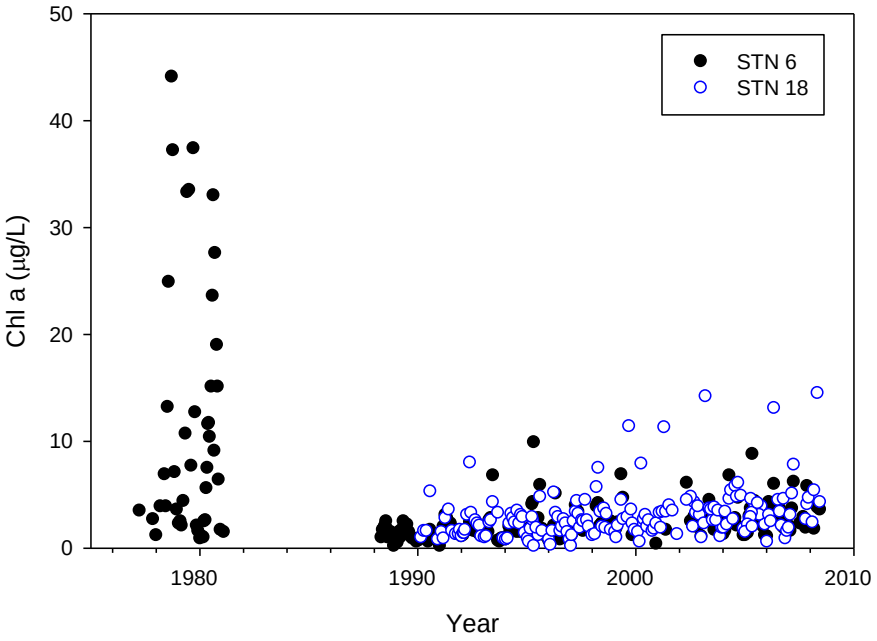


Figure 2-1 **Long-term chlorophyll a concentrations in Suisun Bay (STN 6) and Central Bay (STN 18).**

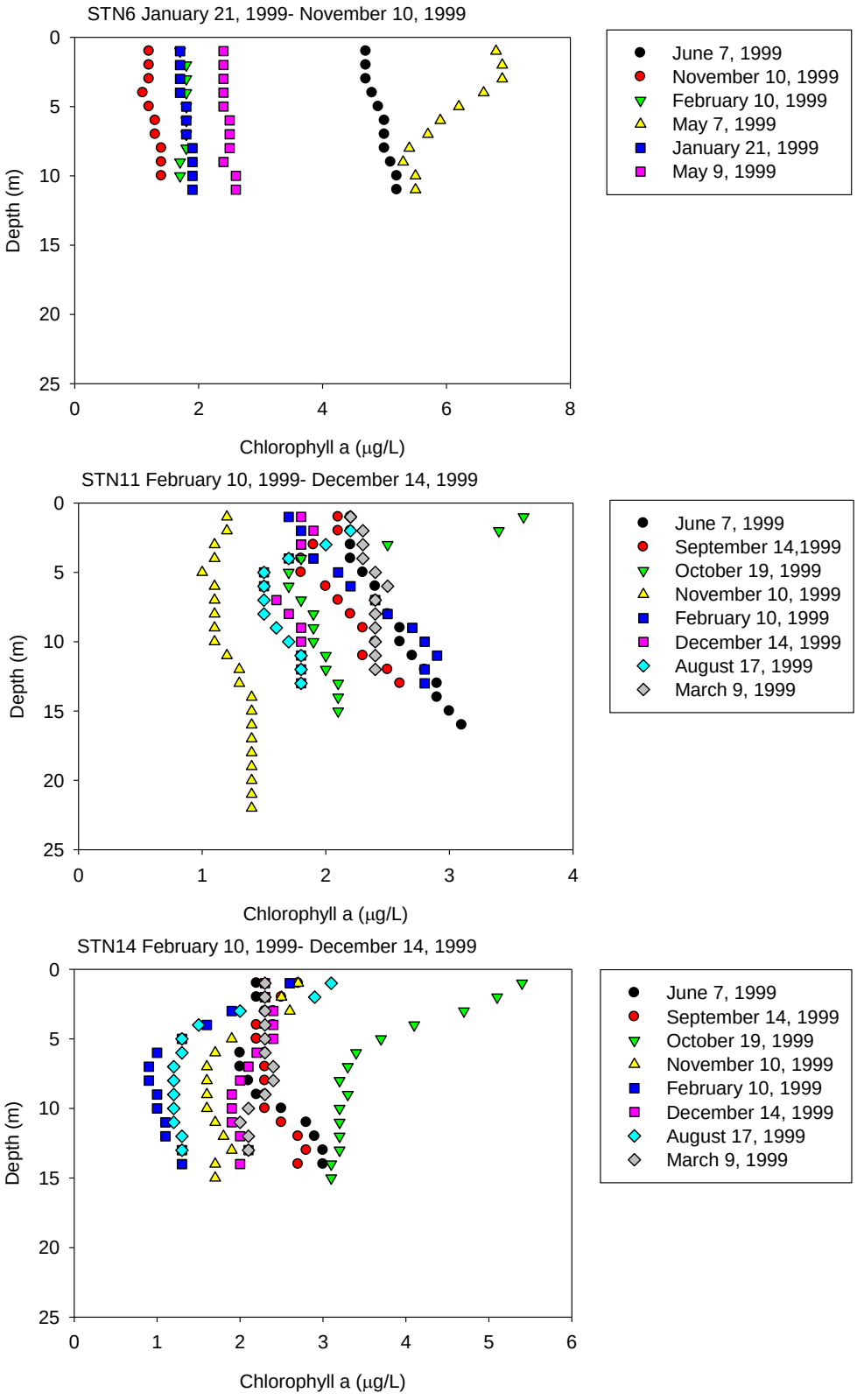


Figure 2-2 **Depth profiles of chlorophyll a concentrations at stations STN 6, STN 11 and STN 14 for year 1999.**

For the application in the NSFB, phytoplankton dynamics are affected by transport, growth, grazing by zooplankton and benthic organisms, settling, respiration and riverine input (Meseck, 2002).

$$\frac{\partial B}{\partial t} = -U\frac{\partial B}{\partial x} + Kx\frac{\partial^2 B}{\partial x^2} + \mu_n B - GB - P_b B - \frac{\partial}{\partial z}(wsB) - RB + B_{river} \quad (10)$$

Where B is the phytoplankton biomass (mg/l), μ_n is net biomass-specific growth rate (d^{-1}), G is the grazing due to zooplankton (d^{-1}), P_b is the benthic grazing rate (d^{-1}), ws is the sinking velocity of phytoplankton (d^{-1}), R is the respiration rate (d^{-1}) and B_{river} is the riverine input of phytoplankton (mg/l/day). Sinking of phytoplankton was found to be between 0.5 – 0.9 m/d and is set to be at 0.5 m/d (Cloern 1991; Kosseff et al. 1993; Lucas et al. 1998). Phytoplankton mortality is due to respiration losses and grazing effects. Mortality due to respiration can be up to 10% of the maximum rate of photosynthesis and is held constant at this value in the model (P_m; mg C/mg Chl/d, Cole and Cloern, 1984). The benthic grazing rate was mostly due to benthic clams such as *Corbula amurensis* after the introduction in 1985. Based on studies by Werner and Hollibaugh (1993), *C. amurensis* has the potential to graze phytoplankton at rates greater than the specific growth rate of phytoplankton and was specified at a constant rate of 0.04 d^{-1}. Benthic grazing rates were found to vary across season and location (Thomspson et al. 2008). Grazing by zooplankton is simulated as a function of zooplankton abundance and ingestion rates of phytoplankton per animal based on weight (Cloern et al, 1985; Appendix 2). Zooplankton abundance varies with space and time and ranges between 13 – 330 organisms/liter (Figure 2-3). The weight of zooplankton ranges from 7 to 63 μg C/organism (Hutchinson, 1981).

The growth rate of phytoplankton is a function of light (Platt and Jassby, 1976). The biomass-specific rate of photosynthesis is modeled as:

$$P = P_m \tanh(\alpha I) \quad (11)$$

where P_m is the maximum rate of photosynthesis at optimal light intensity (mg C/mg Chl/d), α is the initial slope of the light-saturation curve divided by P_m (m^2 d/Einst), and I is the photosynthetically active radiation (PAR, Einst/m^2/d). In the northern reach, P_m varies from 24 to 219 mg C/mg Chl/d (Cloern and Alpine, 1991). The values of α varies from 0.002 to 0.009 Einst.m^2/d (Lucas et al., 1998). Net biomass specific growth rate u_n is simulated as P divided by carbon chlorophyll a ratio. Irradiance of light at depth z is modeled as:

$$I(z) = I_\lambda e^{-kz} \quad (12)$$

where k is the attenuation coefficient of light within the water column (m^{-1}) and z is water depth (m; Miller and Zepp, 1979). In a well-mixed water column the irradiation can be simulated as:

$$I = I_\lambda\left(\frac{1-e^{-kz}}{kz}\right) \quad (13)$$

The attenuation coefficient k is defined as:

$$k = k_w + k_d + k_p + k_s * TSM \quad (14)$$

where k_w is the scattering of light due to water (m^{-1}), k_d is due to dissolved matter (m^{-1}), k_p is due to phytoplankton (m^{-1}), and k_s is due to non-living suspended material (L/g/m). The sum of k_w and k_d is set to 0.1 m^{-1} based on calculations by Miller and Zepp (1979).

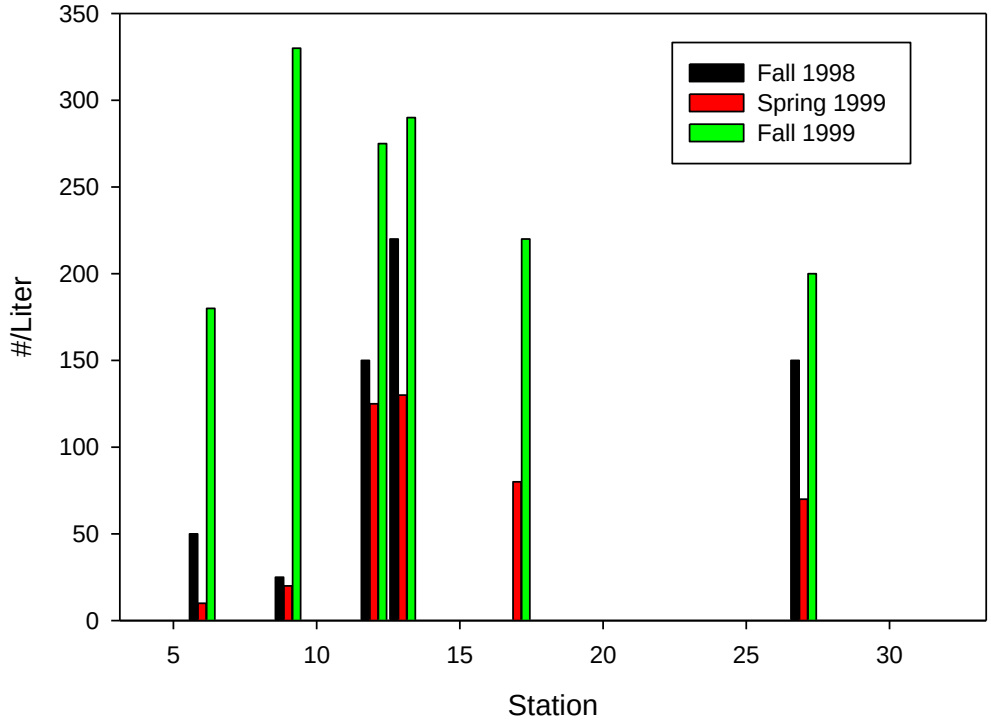


Figure 2-3 Zooplankton abundance sampled by Pukerson et al. (2003) for stations across the Bay.

2.4. DISSOLVED SELENIUM

Dissolved selenium can enter the NSFB from the Delta, local tributaries, refineries, municipal and industrial wastewater discharges, and sediment diffusion. The sources and potential transformations are shown schematically in Figure 2-4. Speciation of selenium from these sources is generally dominated by selenate (SeVI), followed by organic selenide (Se(-II)) and selenite (Se(IV)). While in the water column, different species of selenium can undergo biological and chemical transformations. Transformations of dissolved selenite include oxidation to selenate, uptake by phytoplankton and adsorption and desorption from minerals. Transformations of dissolved organic selenide include oxidation to selenite and uptake by phytoplankton. Dissolved organic selenide is also generated through mineralization of particulate organic selenide. For selenate, the transformation includes uptake by phytoplankton and microbes. Oxidation of selenite to selenate was found to be a slow process which can take hundreds of years, while oxidation of organic selenide to

selenite occurs over a timeframe of weeks (Cutter, 1992). Phytoplankton uptake of dissolved selenium, particularly for selenite, was found to occur relatively rapidly (Riedel et al. 1996; Baines et al. 2004). Uptake of organic selenide was found to occur at approximately at the same rate with selenite, followed by selenate. Data on microbial population and uptake of selenium are not available in the bay.

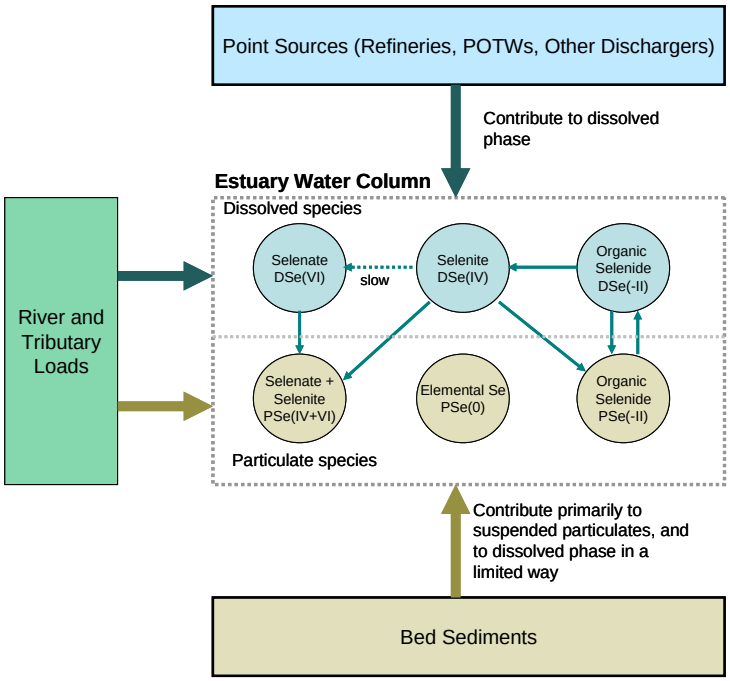


Figure 2-4 **Schematic of selenium sources and transformations in the water column of the estuary. Point sources are primarily in the dissolved form, and sediment erosion contributes mostly to suspended particulates. River and tributary loads can include both dissolved and particulate selenium.**

Dissolved selenium dynamics are modeled as a result of point and non-point source inputs, advection and dispersion, as well as *in situ* transformation. Transformations between species such as oxidation and uptake by phytoplankton are simulated as first-order kinetic reactions. Transformation processes of different species of selenium modeled are:

$$\frac{\partial DSe(VI)}{\partial t} = k_3[DSe(IV)] - k_5[DSe(VI)] + \mathrm{b[PSe(IV)]} - \mathrm{a[DSe(IV)]} \quad (15)$$

$$\frac{\partial DSe(IV)}{\partial t} = k_2[DSe(-II)] - k_3[DSe(IV)] - k_4[DSe(IV)] \quad (16)$$

$$\frac{\partial DSe(-II)}{\partial t} = k_1[PSe(-II)] - k_2[DSe(-II)] - k_6[DSe(-II)] \quad (17)$$

where the rate constant k_1 is the mineralization rate of particulate organic selenide to form dissolved organic selenide. Mineralization of organic selenide was found in a previous study to be a pseudo first-order (Cutter and Bruland, 1984). Rate constants k_2 and k_3 are for

oxidation of organic selenide to selenite and selenite to selenate respectively. Constants k_4 - k_6 are used to model phytoplankton uptake of selenite, selenate and organic selenide, respectively. *D* and *P* refer to dissolved and particulate phases in the water column, and *a'* and *b* relate to adsorption/desorption processes. The uptake and transformation processes are shown schematically in Figure 2-5. For some reactions, a wide range of rate constants was reported in literature, and therefore calibration was needed as described in Section 3. Table 2-1 lists values for the rate constants reported in the literature. Note that rates of uptake from Riedel et al. (1996) and Baines et al. (2004) are absolute rates measured under very different ambient selenite concentrations (10 µg/L and 0.02 µg/L). The uptake rates are shown in Table 2-1 as both absolute rates used in the original references and as uptake rate constants (l/g chl a/hr, in parentheses). The uptake rate constants are not dependent on ambient selenium concentrations. The uptake rates are shown for easy comparison to the original references and for comparison across the two literature sources.

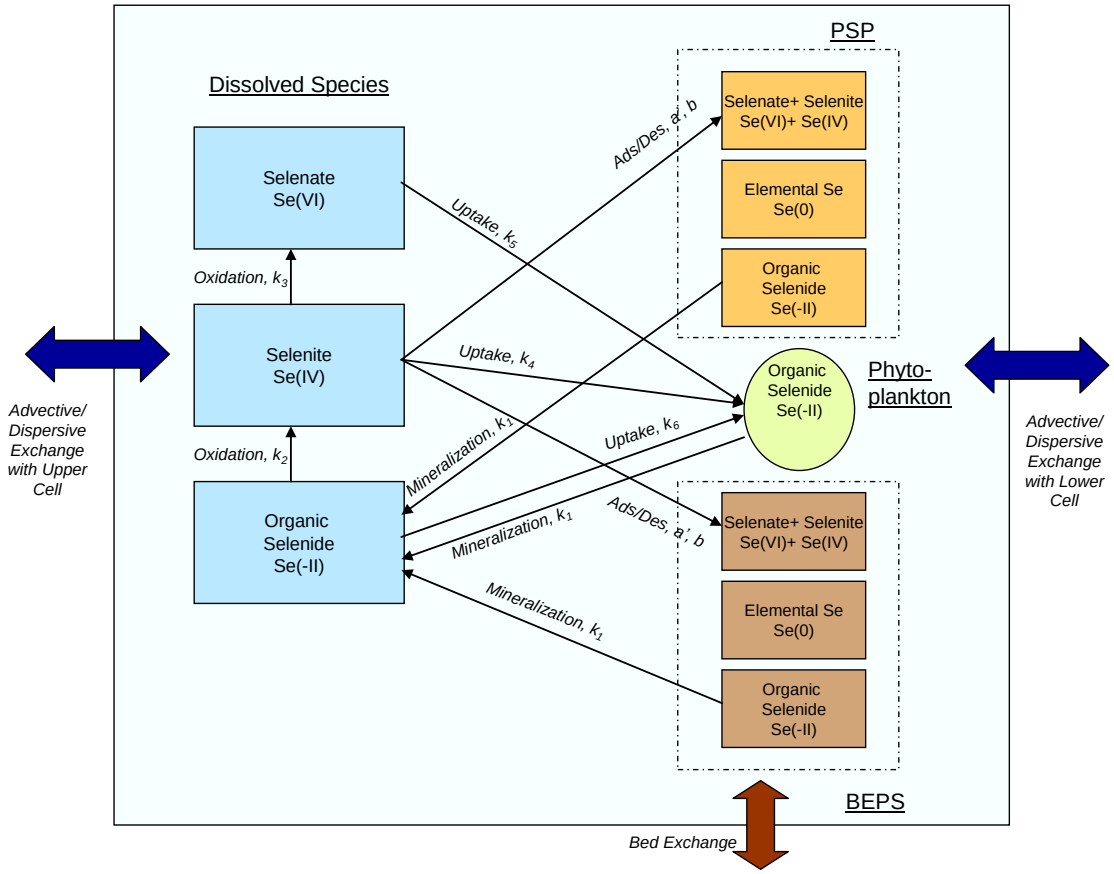


Figure 2-5 **Representation of selenium exchanges between different compartments in each cell of the model. Transformations are shown for each species in the dissolved and particulate phases (PSP, permanently suspended particulates; phytoplankton; and BEPS, bed exchangeable particles).**

Table 2-1
Literature values for first order rate constants

Constant	Process	Description	Value	Unit	Reference
k_1	P Se(-II) → D Se(-II)	Mineralization of particulate organic selenide	1.3×10^{-5}-5×10^{-2}	d^{-1}	Regeneration experiments (Cutter, 1992)
k_2	D Se(-II) → D Se (IV)	Oxidation of dissolved organic selenide	1.0×10^{-3} - 81.0	d^{-1}	Surface and deep Pacific water (Suzuki et al. 1979, cited in Cutter, 1992)
k_3	D Se(IV) → D Se (VI)	Oxidation of dissolved selenite	2.4×10^{-6}	d^{-1}	Deep Pacific, Cutter and Bruland (1984)
k_4	D Se(IV) → P Se (-II)	Uptake of dissolved selenite by phytoplankton	2.02-2.41 (15.8-18.8) 0.07-0.21* (225.8-777.8)*	μmol Se (g chl)$^{-1}$hr^{-1} (l/g chl a/hr) pmol Se (ug chl)$^{-1}$hr^{-1} (l/g chl a/hr)	Riedel et al. (1996) Baines et al. (2004)
k_5	D Se(VI) → P Se (-II)	Uptake of dissolved selenate by phytoplankton	0.43-0.58	μmol (g chl)$^{-1}$hr^{-1}	Riedel et al. (1996)
k_6	D Se(-II) → P Se (-II)	Uptake of dissolved organic selenide by phytoplankton	0.5 k_4	μmol (g chl)$^{-1}$hr^{-1}	Baines et al. (2001)
a'	D Se(IV)_ → PSe (IV)	Mineral adsorption of selenite	0.1-0.8	l/g/d	Zhang and Sparks (1990)
b	PSe(IV) → D Se(IV)	Desorption of adsorbed selenite	Kd/a'	d^{-1}	Zhang and Sparks (1990)

* Values taken are measured rates for two sites (Channel and Chlorophyll maximum) during evening and morning, excluding abiotic uptake in the dark.

Sediment diffusion of selenium was found to be a very small flux based on estimates from Meseck (2002). In the study, fluxes from sediments were estimated as a function of diffusion coefficient and measured concentration gradient in pore water, as well as irrigation by bivalves. In Meseck (2002), the following equation was used in estimating the sediment diffusion:

$$J = - \Phi * D_S * \delta Se/\delta z + \Sigma Z_i \lambda_i (C_w - C_i) \quad (18)$$

Where J is the sediment diffusion flux (nmol/cm^2/yr), Φ is the porosity, D_s is the effective diffusion coefficient (5.83×10^{-6} cm^2 s^{-1}), $\delta Se/\delta z$ is the observed concentration gradient of pore water selenium, z_i is the depth of sediment zone i (2 cm), λ_i is the irrigation coefficient (s^{-1}; 20×10^{-7} s^{-1}), C_w is the overlying water concentration, and C_i is the average pore water concentration at depth *i*. Total selenium fluxes to water column were estimated to be

relatively small. A recent update of the study suggests the flux of selenate was into the sediment at a rate of 0.01 nmol/cm^2/yr (S. Meseck, personal communication).

2.5. PARTICULATE SELENIUM

Particulate selenium may be present in the following forms: particulate elemental selenium, adsorbed selenite and selenate and particulate organic selenide. Particulate selenium in the estuary can originate from riverine input, sediment resuspension, and in-situ transformation. A large amount of sediments and living/non living particulate organic material enters the bay through the rivers. Sediment loads from the Delta were estimated previously by McKee et al. (2006) to range from 0.26 to 2.6 million tons/yr. Different species of particulate selenium are assumed to be associated with PSP and BEPS. Phytoplankton selenium is assumed to be present only as organic selenide. Riverine inputs of particulate selenium are specified as selenium content by different species on riverine loads of particulates (PSP, BEPS, and phytoplankton). Although phytoplankton can be measured as part of the TSM, here phytoplankton is modeled separately and as is the phytoplankton-associated particulate organic selenium. Particulate organic selenium associated with PSP is assumed to be selenium associated with organic carbon other than living phytoplankton (e.g., detritus of phytoplankton, plant material, bacteria).

Selenium contents on riverine PSP are calibrated parameters that are bounded by values in Doblin et al. (2006). Selenium contents on riverine phytoplankton uptake are specified at 15.9 μg/g Se:C (Baines et al. 2004). The value was measured as the uptake ratio of selenite and carbon by plankton from incubation experiments using water collected from a site in the Delta. Particulate selenium associated with BEPS is subjected to exchange with particulate selenium in bed sediments at the same rates of sediment resuspension and deposition. Seawater end member concentrations of particulate selenium are specified as constants (as selenium content on seawater concentrations of PSP) for an open boundary. The transfer from dissolved selenium to particulate selenium includes mineral adsorption (mostly for selenite) and phytoplankton uptake of dissolved selenium for all three dissolved selenium species.

Particulate elemental selenium can be formed through dissimilatory reduction of selenite and selenate in anoxic environments. For NSFB, the water column is oxic, therefore particulate elemental selenium mostly originates from Delta input or in the bed sediment. Particulate elemental selenium is modeled as a result of riverine input, sediment resuspension, and transport processes, and is not produced in the water column of the bay.

$$\frac{\partial PSe_o}{\partial t} = -U\frac{\partial PSe_o}{\partial x} + K_x\frac{\partial^2 PSe_o}{\partial x^2} + Se_{o,SED} * \frac{\partial BEPS_{riv}}{\partial t} + Se_{o,river} * \frac{\partial PSP_{riv}}{\partial t} \quad (19)$$

For particulate adsorbed selenite and selenate, besides inputs from riverine and exchange with the sediments, particulate selenite and selenate are subject to adsorption/desorption.

$$\frac{\partial PSe_{IV+VI}}{\partial t} = -U\frac{\partial PSe_{IV+VI}}{\partial x} + K_x\frac{\partial^2 PSe_{IV+VI}}{\partial x^2} + Se_{IV+VI,SED} * \frac{\partial BEPS_{riv}}{\partial t} + Se_{IV+Vi,river} * \frac{\partial PSP_{riv}}{\partial t} + a' DSe(IV) - b * PSe_{IV+VI} \quad (20)$$

where *a'* is the intrinsic adsorption rate constant (L/g/d) and *b* is the desorption rate constant (d^{-1}).

The adsorption of selenate is considered to be negligible in the Bay water given the high pH. Most studies on selenite and selenate adsorption and desorption are related to soils (Zhang and Sparks, 1990). Selenate adsorption to mineral surfaces was non site-specific and involves the outer sphere complex. Adsorption of selenite is site specific and involves ligand exchange. Therefore the adsorption of selenate is weaker than that of selenite. Both reactions are dependent on pH, with increasing pH resulting in decrease in selenite adsorption (Neal et al., 1987).. It was found that at pH 6, adsorption of selenate is non-detectable. Due to the high pH in the estuary (>6), adsorption of selenate is minimal and only adsorption of selenite is considered (Meseck, 2002). Selenite adsorption was found to occur rapidly in freshwater (i.e., within 60 seconds; Zhang and Sparks, 1990), while desorption is found to occur at a much slower rate.

Zhang and Sparks (1990) found that a' ranges from 0.1 to 0.8 L/g/d. Desorption rate b can be derived as:

$$b = \frac{a'}{K_d} \tag{21}$$

where K_d is partition coefficient for selenite (L/g). For freshwater, K_d ranges between 0.5 to 2.5 L/g (Zhang and Moore, 1996). K_d for selenite based on data from November 11, 1999 averages at 13.3 L/g. For some trace elements such as cadmium, due to competition for adsorption sites, the adsorption decreases as salinity increases:

$$K_d = K_0 * (S+1)^{-b} \tag{22}$$

where K_0 is the partition coefficient in fresh water where salinity is zero and *b* is coefficient that dictates the rate of decreases with salinity (Bale 1987). For selenite, derived K_d values do not show a significant relationship with salinity, therefore b is set to 0 for selenite adsorption.

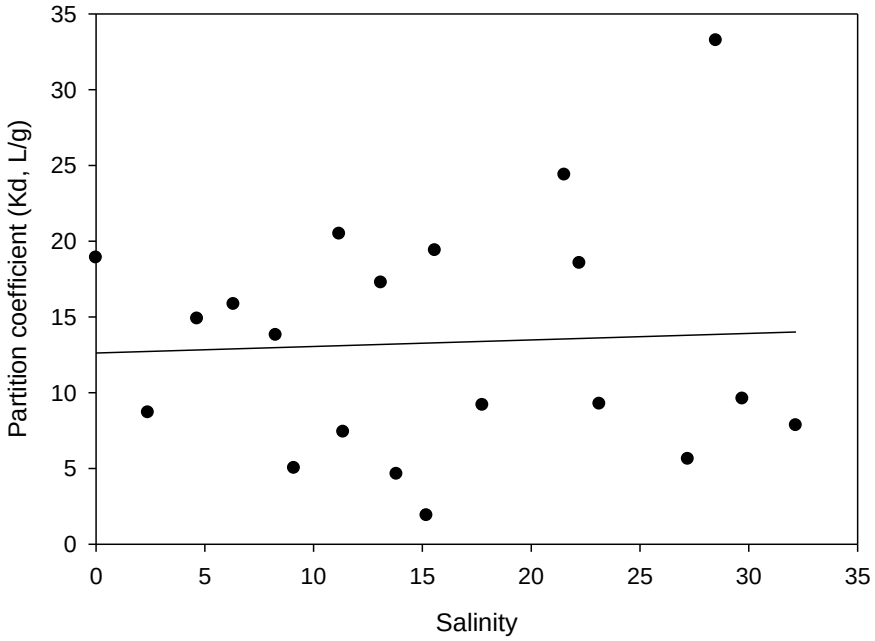


Figure 2-6 Partition coefficient (Kd) of particulate adsorbed selenite and selenate over selenite as a function of salinity in the NSFB (Source: Cutter and Cutter, 2004).

For particulate organic selenium, transformations also include uptake by phytoplankton and mineralization to dissolved organic selenide. Dissolved organic selenide is then oxidized to selenite.

$$\frac{\partial PSe(-II)}{\partial t} = -U\frac{\partial PSe(-II)}{\partial x} + K_x\frac{\partial^2 PSe(-II)}{\partial x^2} + Se_{-II,SED} * \frac{\partial BEPS_{river}}{\partial t} + Se_{-II,river} * \frac{\partial PSP_{river}}{\partial t} \quad (23)$$
$$+ P_{uptake} - k_1[PSe(-II)]$$

Uptake by phytoplankton is calculated as:

$$P_{uptake} = k_4 * [DSe(IV)] + k_5 * [DSe(VI)] + k_6 * [DSe(-II)] \quad (24)$$

Rate constants of phytoplankton uptake and mineralization of particulate organic selenide were discussed previously in Section 2.4. With the kinetic uptake rates by phytoplankton and adsorption/desorption from mineral particulates, the partitioning between dissolved and particulate selenium is modeled as a dynamic process instead of a being defined by a constant partition coefficient.

Selenium in sediments is modeled as a combination of initial concentration modified by resuspension and deposition through sediment-water interaction, as well as some riverine input. The initial concentrations of selenium in sediments by different species were data from Meseck (2002) along the length of the estuary. Sediment concentrations at the surface (<15 cm) were dominated by elemental selenium (60%), followed by organic selenide (20-25%) and particulate selenite and selenate (15-20%). Due to the balanced resuspension and

deposition rates of sediment, the modification of selenium concentrations in bottom sediments is small.

In this document, particulate concentrations are expressed as µg/l or as µg/g depending on the context. The former approach is needed for mass balance type calculations, in that it is a representation of the amount of selenium in a given volume, the latter approach is useful for computing uptake by filter feeders such as bivalves, but without TSM information, does not have any significance in a mass balance calculation.

2.6. SELENIUM UPTAKE BY BACTERIA AND PHYTOPLANKTON

Dissolved selenium in the water column can be directly taken up by phytoplankton and bacteria. Selenium exists in reduced organic forms within algal or bacterial cells or is exuded as dissolved organic selenium. Organic selenium in algal cells is highly bioavailable to organisms that consume them, such as zooplankton and bivalves (Luoma et al., 1992; Schlekat et al., 2000). Therefore, uptake of selenium by bacterial and planktonic organisms is important in evaluating selenium bioaccumulation.

Algal selenium uptake by phytoplankton varies widely across species. Cellular selenium concentrations for nine species of marine algae vary by an order of 10^5 (Baines and Fisher, 2001). Cellular selenium concentrations of various phytoplankton species are shown in Table 2-2. Se:C ratios measured by Doblin et al. (2006) were in atomic units and were converted to µg/g. For NSFB, algal species vary with season and location and over the long term there has been a shift in species (Lehman et al., 2000). In the winter, phytoplankton biomass in the upper estuary is comprised of freshwater diatoms and while in spring blooms marine centric diatoms dominate (Cloern et al., 1985). Over the long-term, there has been a decrease in diatoms and increases in chlorophyte, cyanophyte and flagellates. Recent sampling in 2006-2007 by Lidstrom and Carpenter (2008) also indicated that there have been decreases in diatoms and increases in small cells such as flagellates and picoplankton. Although large variations exist even within the same group (e.g. diatoms show large variations in Se:C ratio across species), selenium concentrations in phytoplankton generally following the order of: golden brown algae> dinoflagellates > diatoms > green algae. The four groups of phytoplankton compared here are used as general groupings. It was also found that phytoplankton during wet and normal years are more dominated by diatoms, green, bluegreen and chrysophytes, while during dry and critically dry years, cryptophytes, green flagellates and miscellaneous flagellates dominate.

During low flow conditions higher salinities could be encountered in the northern parts of the estuary in which freshwater phytoplankton cannot survive. However, under those conditions, marine phytoplankton species are likely to replace freshwater organisms. In this case, freshwater phytoplankton may be mineralized (if not grazed) to dissolved organic selenide, and may be taken up by marine phytoplankton.

The phytoplankton uptake of selenium is treated as one single component and not as two groups of species (marine and freshwater). As long as there is phytoplankton present in the estuary, there is assumed uptake of selenium by phytoplankton.

Table 2-2
Cellular selenium concentrations (ng/µm^3) for marine algae exposed to 0.15 nM (11.84 ng/l) selenite (from Baines and Fisher, 2001; after Abu Saba and Ogle, 2005).

Taxonomic Class	Algal Species	Cellular Se Concentration (ng/µm^3)*	Cellular Carbon Concentration (pg C/µm^3)*	Se:C Ratio (µg/g)*	Particulate Se (µg/g dwt exposed to 90nM Selenite)**
Bacillariophyceae (diatoms)	*Skeletonema costatum*	4.95×10^{-13}	0.14	0.004	3.08
Chlorophyceae (green algae)	*Chlorella autotrophica*	4.73×10^{-11}	0.22	0.215	3.63
Chlorophyceae (green algae)	*Nannochloris atomus*	5.46×10^{-11}	0.22	0.248	3.31
Chlorophyceae (green algae)	*Dunaliella tertiolecta*	1.21×10^{-10}	0.17	0.712	3.87
Bacillariophyceae (diatoms)	*Chaetoceros gracilis*	3.31×10^{-10}	0.14	2.364	3.00
Bacillariophyceae (diatoms)	*Thalassiosira pseudonana*	1.09×10^{-9}	0.16	6.813	5.21
Dinophyceae (dinoflagellates)	*Prorocentrum minimum*	3.08×10^{-9}	0.13	23.692	13.49
Cryptophyceae (golden brown algae)	*Cryptomonas sp.*	4.90×10^{-9}	0.16	30.625	ND
Prymnesiophyceae	*Emiliania huxleyi*	3.37×10^{-8}	0.22	153.182	ND

* Data from Baines and Fisher (2001)

** Data from Doblin et al. 2006converted from atomic ratios to µg/g based on atomic weights of Se (78.9) and C (12).

ND = No data

Selenium uptake exhibits cellular regulation behavior, with cellular selenium concentrations showing less variation corresponding to changes in ambient selenium concentrations in the water column (Baines and Fisher, 2001; Table 2-2). For the diatom *Thalassiosira pseudonana*, the half saturation was found to be at a low concentration of 0.2 nmol/L (0.016 µg/L; Baines and Fisher, 2001). Michaelis-Menton kinetics types of equations can be used in simulating the saturation uptake. However, due to large variations in cellular concentrations among species and the uncertainties in algal species composition in NSFB, the selenium uptake by phytoplankton is modeled using first-order uptake rates without differentiating the algal species, similar to the approach used by Meseck (2002). Model-predicted selenium concentrations in phytoplankton (in terms of Se:C ratio) were compared to observed values in the seston of the Delta (Baines et al., 2004). The Se:C ratio in phytoplankton is calculated as selenium concentrations associated with phytoplankton (µg/L) divided by phytoplankton biomass (in units of carbon, g C/L).

Limited phytoplankton species data for recent years are available from Environmental Monitoring Program (EMP) of Interagency Ecological Program (IEP; http://www.baydelta.water.ca.gov/emp/Stations/station_index.php?station=D41). The data

suggest large variations in species through time and increased flagellates in recent years as shown in a station (D41) in San Pablo Bay, one of the five locations in the Bay sampled for phytoplankton species (Figure 2-7). For station D41, phytoplankton species were dominated by flagellates in recent years of 1999-2003 and by golden brown algae and green algae for 2004-2006 (Figure 2-6). Selenium concentrations in phytoplankton when dominated by green algae are likely to be lower than when dominated by golden brown algae. Cellular selenium concentrations in flagellates however have not been measured in previous studies. Three of the phytoplankton species, *Skeletonema costatum* (diatom), *Rhodomonas salina* (cryptophyte) and *Prorocentrum minimum* (dinoflagellate), are important species found in the San Francisco Bay (Lehman 1996).

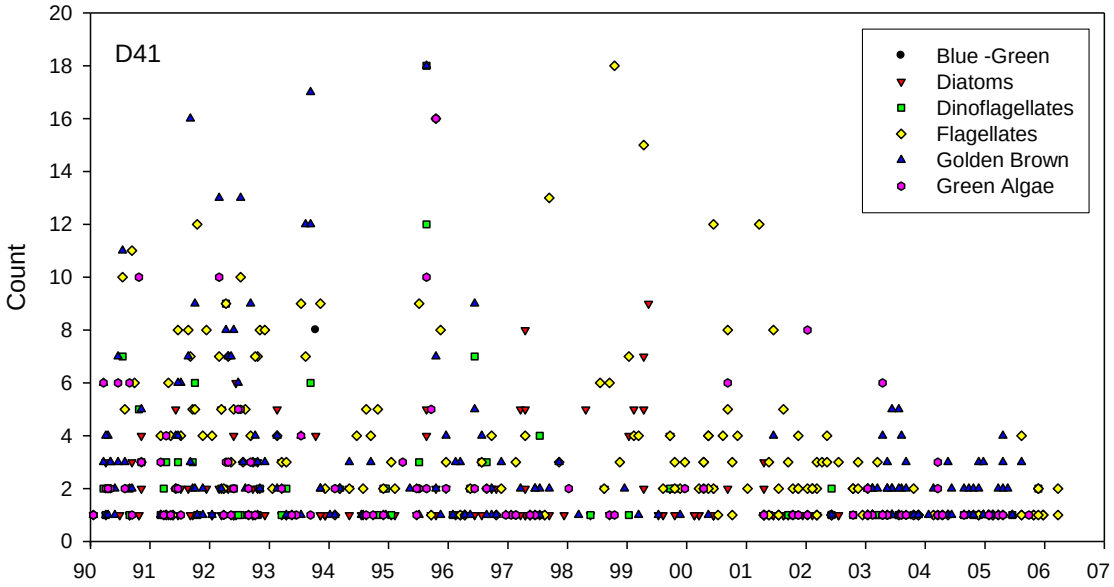


Figure 2-7 Phytoplankton species data from a station in San Pablo Bay (D41) as a function of time (Data Source: IEP).

2.7. SELENIUM UPTAKE BY ZOOPLANKTON AND BIVALVES

Accumulation of selenium to the higher trophic levels through consumption of zooplankton or bivalves has significant implications in the TMDL. Fish that feed on benthic invertebrates were found to accumulate higher concentrations of selenium in their livers (Stewart et al. 2004). Accumulation of selenium in zooplankton or bivalves is mostly through the food-borne route, through the ingestion of particulate selenium (Luoma et al., 1992). Direct uptake of dissolved selenium was found to be minimal. Different origins or different species of particulate selenium differ in the assimilative efficiency to bivalves. Generally, organic-associated particulate selenium such as detritus of phytoplankton or particulate elemental selenium produced through biological reductions are more bioavailable to bivalves than mineral associated particulates (Schlekat et al., 2000).

The modeling of accumulation of selenium in zooplankton or bivalves follows a previously developed metal bioaccumulation model in the bay. The model is the dynamic multi-pathway bioaccumulation model (DYMBAM; Luoma et al., 1992; Stewart et al., 2004;

Presser and Luoma, 2006). The model predicts metal concentrations in bivalve tissues using concentrations in food, food ingestion rate, metal assimilation efficiency, and elimination rate. Parameters for different metals and different species of organisms have been quantified in various studies (reviewed by Luoma and Rainbow, 2005). The filter-feeding *C. amurensis* was found to have higher assimilation efficiency and lower elimination rate, and thus accumulates selenium to higher concentrations than resident bivalves (Lee et al., 2006; Linville et al. 2002).

To predict tissue concentrations in the bivalve *C. amurensis*, the DYMBAM model formulation was added to ECoS. In DYMBAM, accumulation of particulate selenium through lower trophic level organisms is based on dietary and waterborne uptake. The dynamic form of the model is as follows:

$$dCmss/dt = ku \times Cw + AE \times IR \times Cf - ke \times Cmss \quad (25)$$

where Cmss is selenium concentration in tissue (µg/g), ku is the dissolved metal uptake rate constant (L/g/d), Cw is the dissolved metal concentration (µg/L), AE is the assimilation efficiency (%), IR is the ingestion rate (g/g/d), Cf is the metal concentration in food (e.g. phytoplankton, suspended particulate matter, sediment) (µg/g), and ke is the efflux rate (d^{-1}). Uptake through the waterborne pathway was found to be negligible (Luoma et al., 1992). Parameter values of DYMBAM model for uptake of selenium by *C. amurensis* are derived from Stewart et al. (2004; Table 2-3).

Table 2-3
Parameters for DYMBAM model for *Corbula amurensis*

Ku (L/g/d)	*IR* (g/g/d)	*AE* (%)	*Ke* (d^{-1})	Growth Rate (/d)	Tissue Se Concentration (mg/kg)	Reference
0.003	0.25	45-80	0.025		2.1-12.0	Stewart et al. (2004)
0.009	0.1-1.0	36(sediment) 54(algae)	0.023	0.005	3.9-20.0	Lee et al. (2006)

In the model, the steady state formulation of equation (21) is used. The bioaccumulation of bivalves through time can be modeled through integrating the above equation through time with an initial concentration. The results are similar to steady state formulation except for the period of ramping up of the model and therefore the steady state equation is used. AE for different species of particulate selenium for *Corbula amurensis* derived from literature are listed in Table 2-4. Assimilation efficiencies measured by Schlekat et al. (2002) are in a relatively narrow range for different species of algae and are generally high. AE for elemental selenium are generally low, with biogenic particulate elemental selenium showing higher AE. Assimilation efficiency measured by Lee et al. (2006) for algae was at a lower value of 54%, which may be due to low spiked selenium concentrations used in algae (two orders of magnitude lower than that observed in SFB waters) and mixture of sediment with algae in the food. Different ingestion rates have also been estimated for *Corbula amurensis*. The ingestion rates estimated by Lee et al. (2006) show a wide range of 0.1 to 1.0 g/g/day (Table 2-3). The ranges in assimilation efficiency and ingestion rates were used to forecast the range of selenium concentrations in bivalves (Table 2-5 and Box 1). In the model

predictions of different scenarios, an AE of 0.2 or 20% was used for particulate elemental selenium. An AE of 45% was used for particulate adsorbed selenite + selenate, and an AE of 80% was used for particulate organic selenium. Ingestion rates used in model predictions range between 0.25 to 0.85 g/g/day (Table 2-5) and an ingestion rate of 0.45 g/g/day was used in model scenario predictions. Assimilation efficiency for particulate organic selenium has generally been determined using living phytoplankton although tests with sediments have also been performed.

Table 2-4
Literature values of assimilation efficiencies (AE) for Corbula amurensis

Species	AE	Origin	Reference
Se(0)[2]	2%	AA – reduction of SeO_3^{2-} to Se(0) through ascorbic acid (AA)	Schlekat et al. (2000)
Se(0)	7 ± 1%	SES – reduction of SeO_3^{2-} to Se(0) through pure bacteria culture (SES)	Schlekat et al. (2000)
Se(0)	28 ± 15%	SED – reduction of SeO_3^{2-} to Se(0) through sediment microbial consortium (SED), biogenic origin	Schlekat et al. (2000)
Selenoanions	11%	Reoxidized sediment slurries	Schlekat et al. (2000)
Organoselenium	53%	Ph. Tricornutum	Schlekat et al. (2000)
Cryptomonas sp.	88.9%	Algae cells	Schlekat et al. (2002)
Gymnodinium sanguinem	82.6%	Algae cells	Schlekat et al. (2002)
Phaeodactylum tricornutum	80%	Algae cells	Schlekat et al. (2002)
Synechococcus sp.	78.3%	Algae cells	Schlekat et al. (2002)
Thalassiosira pseudonana	87.3%	Algae cells	Schlekat et al. (2002)
Sediment	36%	Fresh water stream, San Jose, CA	Lee et al. (2006)
Algae (mixed with sediment)	54%	Diatan, Phaeodactylum tricornutum	Lee et al. (2006)

Table 2-5
Parameters for DYMBAM Model Used in Model Simulations

Parameter Set	IR	AE (particulate elemental selenium, PSe0)	AE (particulate adsorbed selenite and selenate, PSeivvi)	AE (particulate organic selenide, POrgSe)
1	0.45	0.2	0.45	0.8
2	0.25	0.2	0.45	0.8
3	0.45	0.2	0.45	0.54
4	0.85	0.2	0.45	0.80

[2] This form of elemental selenium does not occur in nature and was synthesized in the laboratory.

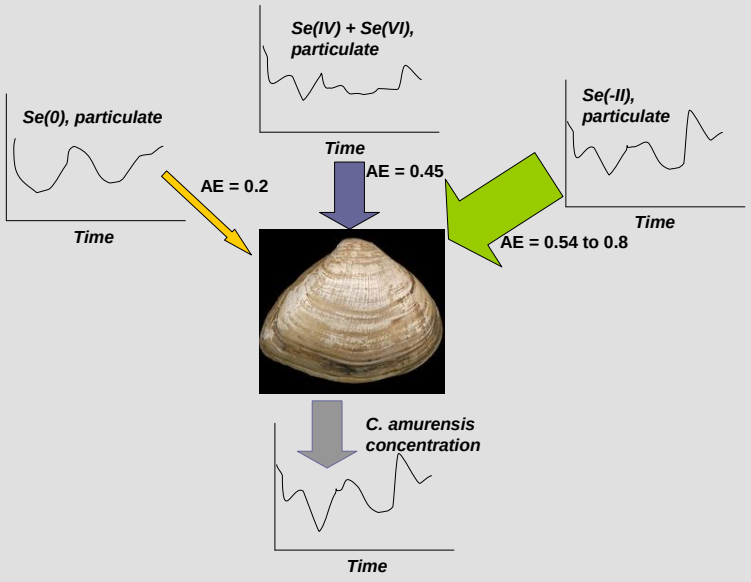
The DYMBAM approach has been found to predict selenium concentrations in clams (*Macoma balthica*) relatively well (Luoma et al., 1992). The use of this approach in predicting selenium concentrations in the mussel *Mytilus edulis* also show good agreement (Wang et al., 1996). Selenium concentrations in the bivalve *Corbula amurensis* were found to vary seasonally, with higher concentrations during low flow (Linville et al., 2002). Particulate selenium concentrations were also found to be higher during low flow. The linear relationship between selenium concentration in food and tissue concentrations as suggested in DYMBAM is considered as applicable in predicting selenium accumulation in this bivalve. Parameters for bioaccumulation of selenium through zooplankton were determined previously for NSFB as listed in the following table (Table 2-6).

Table 2-6
Parameters for DYMBAM Model for Zooplankton (Stewart et al. 2004)

Food Chain (species)	Ku (L/g/d)	IR (g/g/d)	AE (%)	Ke (d^{-1})	Tissue Se Concentration (mg/kg)	Reference
Mysid Copepods	0.024	0.42	50-53	0.155	0.7-2.2	Stewart et al. (2004)
N. Mercedis	0.027	0.45	73	0.25	0.9-2.7	Stewart et al. (2004)

Box 1. Selenium Uptake by Bivalves

In the model formulation, clams derive their selenium entirely from the different particulate phases, based on laboratory data that show minimal direct uptake of dissolved phase selenium (Luoma et al., 1992). Furthermore, the assimilation efficiency of uptake of particulate selenium varies by species. For Corbula amurensis, the species focused on in this work, laboratory data have shown that the highest efficiency of uptake is for selenium associated with algae or organic matter (present as selenides, or Se(-II)), and the lowest for particulate elemental selenium (Se(0)), with particulate inorganic selenium (Se(IV)+Se(VI)) efficiency somewhere in between (Schelkat et al., 2000, 2002; Lee et al., 2006). The model is set up to relate selenium uptake in clams to the simulated concentration of each of these particulate species as shown below. Clam concentrations can change over time, as a result of varying particulate concentrations.



2.7.1 Selenium Uptake by Higher Trophic Organisms

In NSFB, the most significant pathway of selenium bioaccumulation to the higher trophic level is through the benthic-feeding species. Building on the discussion presented in previous sections, the schematic of the processes leading to bioaccumulation in predator organisms is shown schematically in Figure 2-8. The primary organisms that fit this category are benthic-feeding fish, such as the white sturgeon (*Acipenser transmontanus*) and diving ducks (Lesser scaup, *Aythya affinis*; Greater scaup, *Aythya marila*; Surf scoter, *Melanitta perspicillata*). Concentrations in liver and muscle tissues of sturgeon and diving ducks have been measured in previous studies in the bay and in the San Joaquin Valley (White et al., 1987, 1988, 1989; Stewart et al. 2004; SFEI 2006).

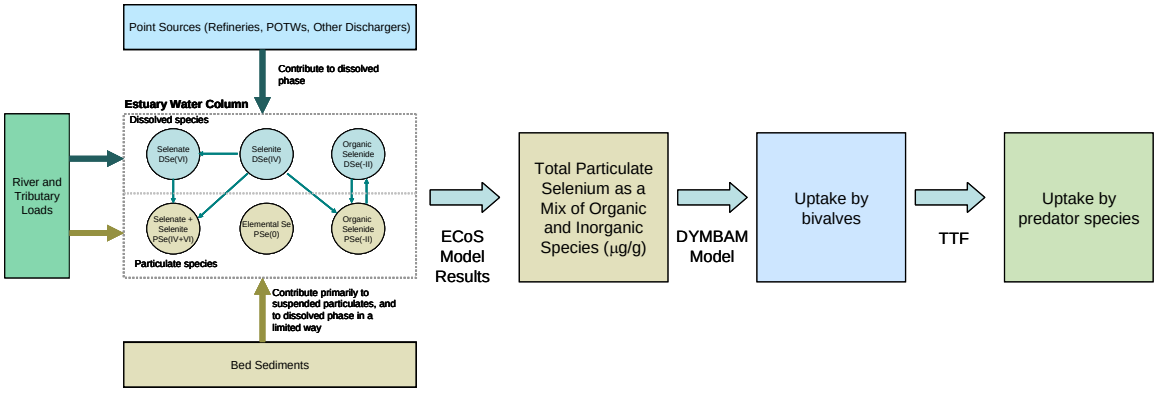


Figure 2-8 **Schematic of selenium transfers from the water column and suspended particulates to bivalves, and then to predator species. The selenium sources and water column transformations are discussed in Sections 2.4, 2.5, and 2.6. Note that once selenium is bioaccumulated by bivalves, and present largely in the organic form, speciation is not a consideration in further uptake by predator species.**

The transfer of selenium to higher trophic levels can be represented through relationships between dietary and tissue concentrations as measured in the field, or using exposures based on more general relationships between ingestion and body weight, or with literature estimates of trophic transfer factors (TTFs) which are ratios of diet concentrations to tissue concentrations. All three methods are described below.

2.7.2 Linear Relationships Using Field Data

Presser and Luoma (2006) developed linear relationships between concentrations in bivalves and predators (scaup, surf scoter, and sturgeon), using data sampled for the same location and time. Data for *C. amurensis* are lacking for years before 1995 and therefore concentrations for *Corbicula fluminea* for these years were used. For surf scoter and white sturgeon, derived linear relationships between tissue concentrations in *C. amurensis* and concentrations in predators are based on previous studies of Presser and Luoma (2006):

$$Csurf\ (liver) = 19.28\ Cmss - 2.35\ (R^2 = 0.86) \quad (26)$$

$$Csturgeon\ (liver) = 3.15\ Cmss - 3.50\ (R^2 = 0.91) \quad (27)$$

$$Csturgeon\ (flesh) = 1.68\ Cmss + 1.04\ (R^2 = 0.66),\ \text{Corbicula only} \quad (28)$$

where *Cmss* are concentrations in bivalves (µg/g), and *Csurf* (liver) and *Csturgeon* (liver) are concentrations in livers of surf scoter and white sturgeon. Equations for predicting concentrations in tissue were not reported for *C. amurensis*, and are shown only for *C. fluminea*. The relationship predicts a concentration of 209.7 µg/g-dwt in surf scoter liver and 31.2 µg/g-dwt in white sturgeon liver, given an average bivalve concentration of 11 µg/g (Linville et al. 2002; Stewart et al. 2004). Data for selenium concentrations in surf scoter liver are lacking for recent years. Average concentration in white sturgeon liver is 24.1 µg/g-dwt in the Bay, suggested by data collected by SFEI and USGS in 2000 and 2001. The linear relationships above are currently used in the model calculations.

2.7.3 Selenium exposures based on food ingestion

The exposure of a contaminant of potential ecological concern (COPEC) for birds and mammals can be calculated using pathway-specific exposure equations of the general form:

$$Exposure = \frac{EPC \times CR \times FC}{BW} \tag{29}$$

where:

EPC = exposure point concentration; the concentration of a COPEC in media that is likely to be contacted by receptors of concern.

CR = contact rates or intake rates; including ingestion and drinking rates.

FC = fraction of media contacted; including site presence index and diet portions.

BW = body weight of the receptor.

Exposure equations used in this approach are consistent with federal and state guidance (DTSC 1996a,b; U.S. EPA 1989b, 1993). The total exposure to each COPEC for birds was calculated as the sum of exposure via water ingestion, sediment ingestion, and the ingestion of food items. This can also be written as follows:

Exposure Dose = Exposure from water ingestion + Exposure from sediment ingestion + Exposure from food ingestion

Putting this equation in the form of the general equation given above for calculating exposure, the following equation is produced:

$$\text{Exposure dose} = \left[\frac{\text{EPC}_{\text{water}} \times \text{DR} \times \text{FC}}{\text{BW}}\right] + \left[\frac{\text{EPC}_{\text{sediment}} \times \text{IR} \times \text{FC} \times \text{SPI}}{\text{BW}}\right] + \left[\frac{\text{EPC}_{\text{tissue}} \times \text{IR} \times \text{FC} \times \text{SPI}}{\text{BW}}\right] \tag{30}$$

where:

EPC_{water} = EPC for a COPEC in water (in µg/L);

$EPC_{sediment}$ = EPC for a COPEC in sediment (in mg/kg);

EPC_{tissue} = EPC for a COPEC in plant, invertebrate, or fish tissues (mg/kg);

DR = Drinking, or surface water ingestion, rate (ml/day);

IR = Ingestion rate of sediment or food (mg/day);

FC = Fraction contacted (unitless; assumed to be 1);

SPI = Site presence index (unitless; assumed to be 1); and

BW = Body weight (kg).

Exposure factors were derived following the approach used by the Wildlife Exposure Factors handbook (U.S. EPA 1993), using primary literature sources.

The effects assessment identifies and quantifies potential adverse effects caused by exposures to the COPECs at the site and, where possible, evaluates cause-and-effect relationships (U.S. EPA 1992a). Potential adverse effects are quantitatively calculated as Hazard Quotients (HQs), which are estimated by dividing a receptor's exposure to a COPEC by the COPEC's TRV; i.e.,

$$HQ = \frac{Exposure}{TRV} \tag{31}$$

where:

HQ = Hazard quotient

TRV = Toxicity reference value

The toxicity reference value was based on a study of mallards performed by Heinz et al. (1989).

Allometric scaling factors were also used to adjust doses when the test species was not the same as the receptor species evaluated (Sample and Arenal 1999). These factors adjust for differences in body weight, metabolism, pharmacokinetics, and sensitivity to provide the best available estimates of species-specific toxicity.

The equation used for adjusting doses with allometric scaling factors is (Sample and Arenal 1999):

$$A_w = A_t \times \left(\frac{BW_t}{BW_w} \right)^{(1-b)} \tag{32}$$

Where:

A_w = Toxicity value for a particular wildlife species;

A_t = Toxicity value for the test species;

BW_t = Body weight of the test species;

BW_w = Body weight of wildlife species; and

b = Allometric scaling factor provided by Sample and Arenal (1999).

Derived TRV values for three species: Surf Scoter, Greater and Lesser Scaup are shown in Table 2-7.

Table 2-7
Body Weight and TRV Values for Test and Wildlife Species

		Body Weight (kg)	Adjusted NOAEL-Equivalent TRV (mg/kg-day)		Source
			Low	High	
Test Species	Mallard Ducks	1.10	0.36	0.73	Heinz et al. 1989
			Allometrically Adjusted TRVs		
Wildlife Species	Surf Scoter	0.90	0.35	0.70	Calculated
	Greater Scaup	0.96	0.35	0.71	Calculated
	Lesser Scaup	0.79	0.34	0.68	Calculated

Hazard Quotients (HQs) are used to estimate the potential for adverse ecological impacts when exposure and toxicity data are available. An HQ is the ratio of the exposure to the TRV (mg/kg-day):

$$HQ = \frac{Exposure}{TRV} \tag{33}$$

An *HQ* less than 1 indicates that there is a negligible potential for adverse ecological impacts due to exposure to a particular COPEC, whereas an *HQ* greater than 1 indicates that there is a potential for adverse ecological impacts due to exposure to that COPEC. However, there are a number of conservative assumptions that are incorporated in the estimated *HQs* and a value slightly greater than 1 does not indicate significant risk. The conservative assumptions include the consumption only of *Corbula amurensis* (i.e., the diet items with the highest selenium content), the presence of the birds in the bay 100% of the time, and using time series values of dietary concentrations, with periods of high concentrations not averaged out.

For birds and mammals, both NOAEL TRVs and LOAEL TRVs were derived, and were used to calculate corresponding NOAEL HQs and LOAEL HQs. A NOAEL HQ gives a conservative estimate of the comparison between exposure at site conditions and maximum safe exposure levels. A NOAEL HQ less than 1 would indicate that no risks are likely to occur from that particular exposure. The LOAEL HQ represents a comparison of exposure

at site conditions with doses known to result in effects. A LOAEL HQ greater than or equal to 1 would indicate that a potential for risks exists. If the NOAEL HQ is greater than or equal to 1, and the LOAEL HQ is less than 1, a conclusion must be drawn by close evaluation of several factors (e.g., exposure parameters, magnitude of the HQ, source of the TRV, probability of site use by the receptor, and special-status of the receptor).

2.7.4 Trophic Transfer Factors

Recent compilation of data suggests that there is a relatively well defined relationship between concentrations of selenium in organism diets and in their tissues (Presser and Luoma, personal communication, 2009, manuscript under development). A ratio between selenium concentrations in tissue and diet of organisms, Trophic Transfer Factor (TTF) can be used in estimating bioaccumulation of selenium through the food web, once dietary concentrations are known. The ratio can be derived based on kinetic uptake rates or observed concentrations of diet and tissue. For example, TTF for invertebrates can be derived as: TTF = (AE)(IR)/ke, where AE = assimilation efficiency; IR = Ingestion rate, and ke = elimination rate. For most fish species the TTF ranges from 0.9 to 1.1, although higher values of 1.7 have been reported for one data set with white sturgeon. TTFs have also been found to vary with ambient selenium concentration. For the purpose of this calculation, TTFs of 1.1 and 1.7 for white sturgeon are both used. A TTF of 1.8 has been reported for scaup in the estuary from a diet primarily of *C. amurensis* (Presser and Luoma, personal communication, 2009).

2.8. SUMMARY OF MODEL FORMULATION

The combined set of equations used to represent selenium fate and transport, including ancillary parameters such as salinity, suspended solids, phytoplankton, and uptake by clams and predator species is presented in summary form in Box 2. As noted above, the basic equations used in this work are those of Meseck and Cutter (2006), with additions for biological uptake.

Box 2. Model Equations

Salinity

$$\frac{\partial S}{\partial t} = -U\frac{\partial S}{\partial x} + Kw\frac{\partial^2 S}{\partial x^2}$$

TSM

TSM = PSP + BEPS + B

$$Ubeps = d*(U - e*R*S)$$

$$Kbeps = \varepsilon*U + \psi*R*S$$

Phytoplankton

$$\frac{\partial B}{\partial t} = -U\frac{\partial B}{\partial x} + Kx\frac{\partial^2 B}{\partial x^2} + \mu_n B - GB - P_b B - \frac{\partial}{\partial z}(wsB) - RB + B_{river}$$

Dissolved Selenium

$$\frac{\partial DSe(VI)}{\partial t} = k_3[DSe(IV)] - k_5[DSe(VI)] + \text{b[PSe(IV)] - a}'\text{[DSe(IV)]}$$

$$\frac{\partial DSe(IV)}{\partial t} = k_2[DSe(-II)] - k_3[DSe(IV)] - k_4[DSe(IV)]$$

$$\frac{\partial DSe(-II)}{\partial t} = k_1[PSe(-II)] - k_2[DSe(-II)] - k_6[DSe(-II)]$$

Particulate Selenium

$$\frac{\partial PSe_o}{\partial t} = -U\frac{\partial PSe_o}{\partial x} + K_x\frac{\partial^2 PSe_o}{\partial x^2} + Se_{o,SED}*\frac{\partial BEPS_{riv}}{\partial t} + Se_{o,river}*\frac{\partial PSP_{riv}}{\partial t}$$

$$\frac{\partial PSe_{IV+VI}}{\partial t} = -U\frac{\partial PSe_{IV+VI}}{\partial x} + K_x\frac{\partial^2 PSe_{IV+VI}}{\partial x^2} + Se_{IV+VI,SED}*\frac{\partial BEPS_{riv}}{\partial t} + Se_{IV+Vi,river}*\frac{\partial PSP_{riv}}{\partial t} + a'DSe(IV) - b*PSe_{IV+VI}$$

$$\frac{\partial PSe(-II)}{\partial t} = -U\frac{\partial PSe(-II)}{\partial x} + K_x\frac{\partial^2 PSe(-II)}{\partial x^2} + Se_{-II,SED}*\frac{\partial BEPS_{river}}{\partial t} + Se_{-II,river}*\frac{\partial PSP_{river}}{\partial t} + P_{uptake} - k_1[PSe(-II)]$$

Selenium in bivalves

$$dCmss/dt = ku \times Cw + AE \times IR \times Cf - ke \times Cmss$$

Selenium in Fishes/Birds

Csturg = TTFsturg * Cmss
Cscaup = TTFscaup *Cmss

2.9. BOUNDARY CONDITIONS AND EXTERNAL LOAD INPUTS

The definition of boundary conditions is a key step in the solution of the set of coupled differential equations discussed above, and has a major impact on the concentrations of different species that are calculated (see Box 3). This section presents the rationale for the boundary conditions used in this application, which occur primarily at the freshwater and seawater ends. Also related to this definition are the external loads that are added to the estuary in the form of other point sources, local tributary inputs, or input from the South Bay as shown schematically in Figure 2-9.

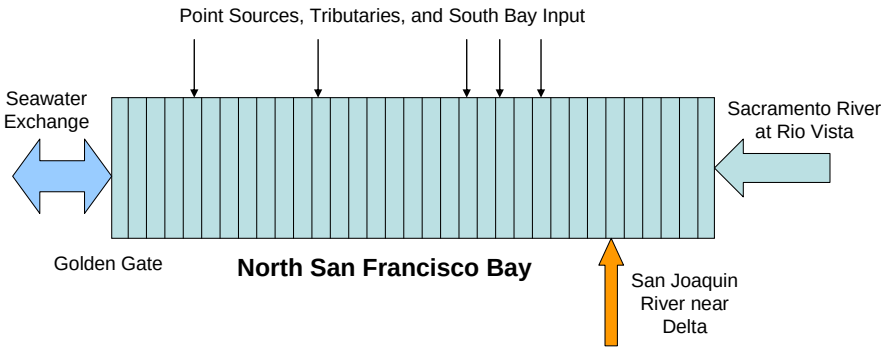
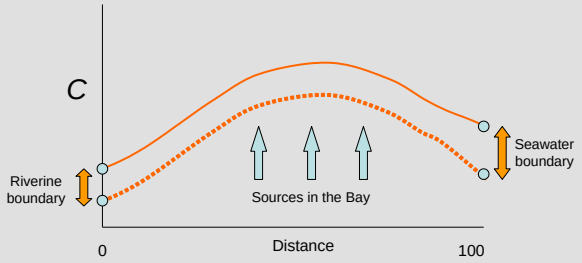


Figure 2-9 **Schematic of model representation of the NSFB, showing model cells or nodes (vertical boxes), boundary conditions, and external loads. Each cell is 3 km wide. The locations of the external loads are illustrative, and are added in the model location at the approximate location they enter the estuary.**

Box 3. Boundary Conditions

Differential equations represent change in space and/or time, and the solution of any differential equation requires the definition of initial and boundary values. In the context of the 1-D simulation of various concentrations over distance through the NSFB, and over time, this refers to initial values of all constituents through the length of the estuary, and concentrations at the freshwater and seawater ends. Together with other inputs along the length of the estuary, such a point sources, local tributaries, and sources from the South Bay, these define the calculated concentrations along the estuary, as shown below. Even when other parameters in the equations stay the same, the boundary conditions can determine the concentrations in the estuary. For this reason, it is important to get an accurate representation of the boundary values, and when these are not well known, to consider a range of values to represent possible conditions in the bay.



In ECoS3, three types of boundary conditions can be specified: closed boundary, open boundary with a set value (boundary concentration) and open boundary with a gradient. An open boundary condition (with seawater end member concentration) is usually used for the estuary mouth. The riverine boundary condition can be specified either as closed boundary or open boundary. When modeled using open boundary, a riverine endmember concentration is needed. In this application, all the solutes except salinity were modeled using a closed riverine boundary condition, with riverine inputs (loads) specified as riverine concentrations multiplied by flow.

Boundary conditions need to be defined for the calibration year (1999), as well as for all years of the simulation, typically 1999-2006 for this application. Boundary conditions were generally defined by measurements for 1999, and either by measurements or through assumptions for subsequent years.

2.9.1 Flow

The riverine flow boundary used is the flow record at the Sacramento River at Rio Vista, obtained from DAYFLOW record from Interagency Ecological Program (IEP; http://www.iep.ca.gov/dayflow/index.html). The San Joaquin River is modeled as a tributary to the estuary, with flow derived as the difference between Net Delta Outflow Index (NDOI) and flow from the Sacramento River at Rio Vista. Figure 2-10 shows the time series of daily outflow from Delta, Sacramento River at Rio Vista and estimated San Joaquin River flow input. Another freshwater input is the direct precipitation on water surface of the bay. Precipitation data were obtained from the California Irrigation Management Information System (CIMIS) for a station near Napa (Station #109). Locations for CIMIS stations around the Bay area are shown in the Appendix (Figure A.4-1). Evaporation loss from the water surface was estimated based on values from Uncles and Peterson (1996) and ranged between 0.95×10^{-8} m/s in December to 6.2×10^{-8} m/s in July.

Simulations presented in this work depend on data availability, but in most cases are for the years 1999 to 2006. There are some exceptions when data are shown for years preceding 1999; this is largely to demonstrate model performance in under different hydrologic regimes. A more complete summary of the inflows from the Sacramento and San Joaquin River watersheds to the Delta, and the hydrologic classification of the water years by the California Department of Water Resources is shown in Figure 2-11.

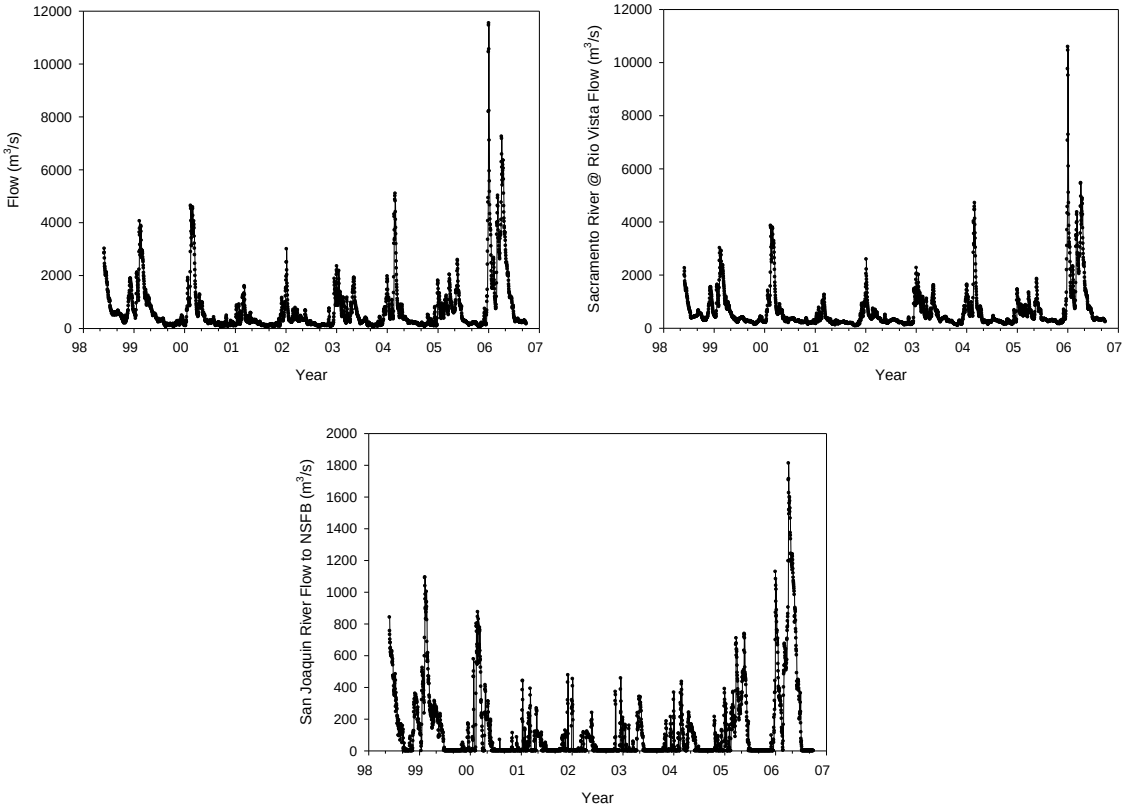


Figure 2-10 **Daily outflow from (a) Delta, (b) Sacramento River at Rio Vista, and (c) San Joaquin River. (Data source: IEP) Note that the y-axis values for San Joaquin River are different, and that during the dry periods of most years, the contribution of San Joaquin River flow to the bay is practically zero.**

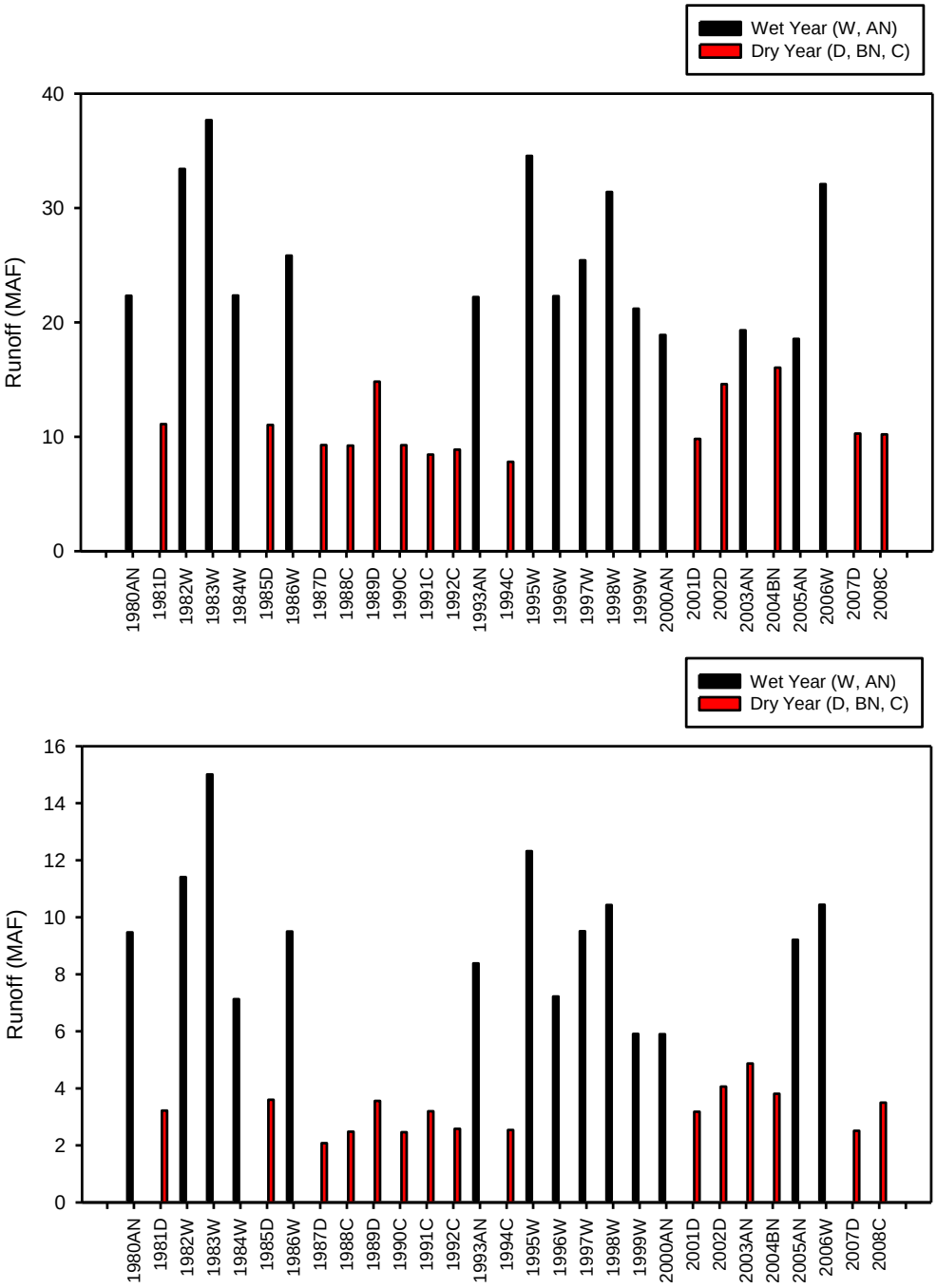


Figure 2-11 Annual flow from the Sacramento and San Joaquin River basins and the hydrologic classification by the California Department of Water Resources.

2.9.2 Total Suspended Material (TSM)

The seawater end member of TSM was specified to be 0.01 g/L and was held constant over the duration of the simulation period.

Riverine inputs of TSM loads were modeled as riverine flow multiplied by concentration, with PSP and BEPS as a fraction of TSM, as in the newest routine of ECoS3 (v3.39; Harris

and Gorley, 1998). Concentrations of TSM from rivers are modeled as a function of river flow, with higher sediment concentrations occurring under high flow (Harris et al. 1984):

$$TSM_{river} = a + b * Q_{sac}{}^{c} \quad (34)$$

where *a* is the minimum concentration in the river water, and *b* and *c* are calibration coefficients. TSM concentrations derived from the above equation compared to the observed concentrations at Rio Vista are shown in Figure 2-12. (r = 0.312). The riverine inputs of TSM loads are derived from flow multiplied by concentrations (Figure 2-13).

The inputs of TSM from the San Joaquin River were modeled as a separate source, with concentrations derived from the equation above based on flow from the San Joaquin River (Figure 2-9) and loads derived from flow multiplied by concentrations (Figure 2-13). The inputs from San Joaquin River were added at the location where San Joaquin River flow enters the estuary (X = 19 km). Note that this approach uses the best representation of TSM data from San Joaquin River near the confluence with the estuary, and these concentrations are different from values upstream at Vernalis, where the San Joaquin River enters the Delta.

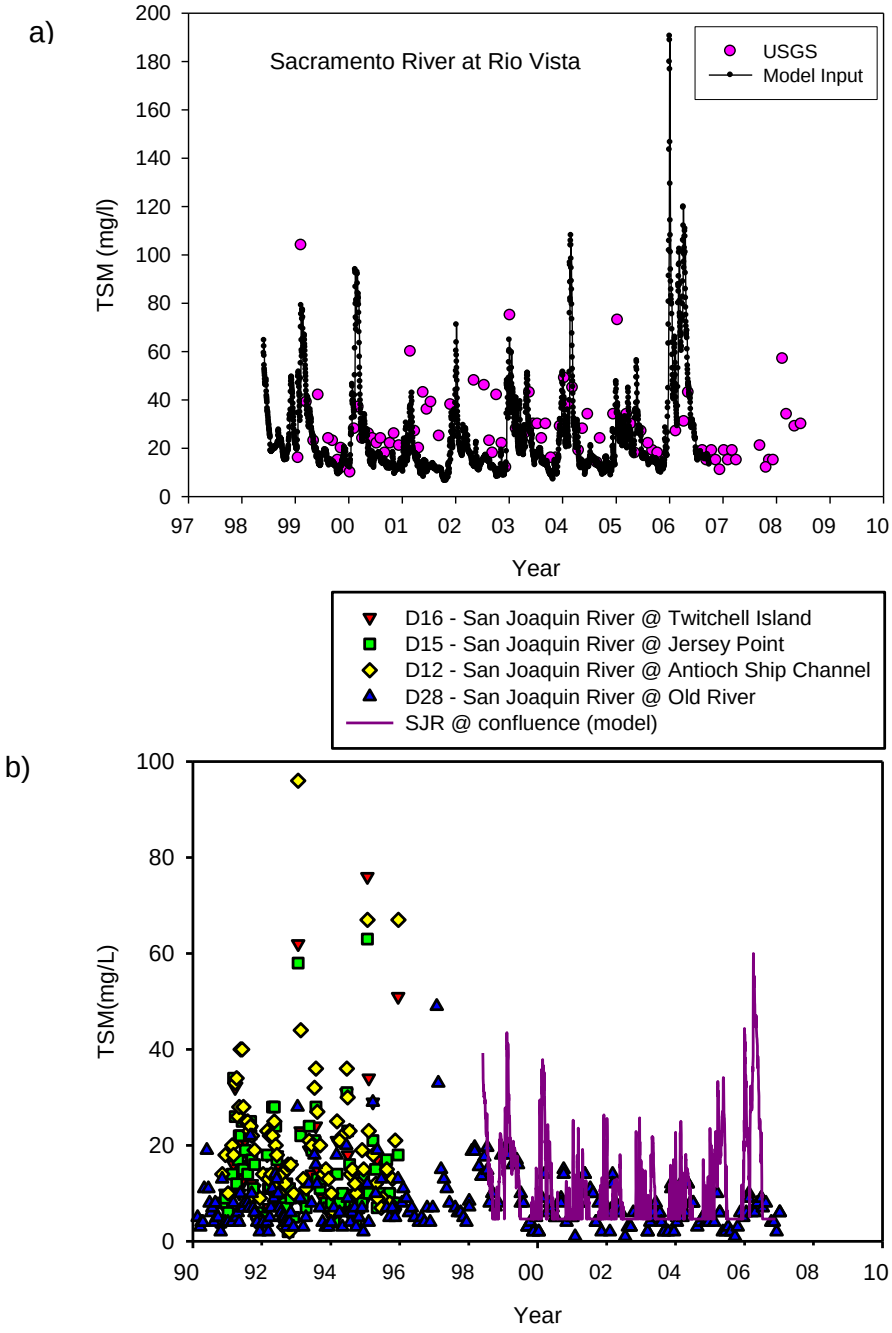


Figure 2-12. **Model inputs of TSM concentrations for (a) Sacramento River at Rio Vista and (b) San Joaquin River at confluence compared to observed values (Data source: USGS). The stations shown for San Joaquin River are in the Delta, downstream of Vernalis.**

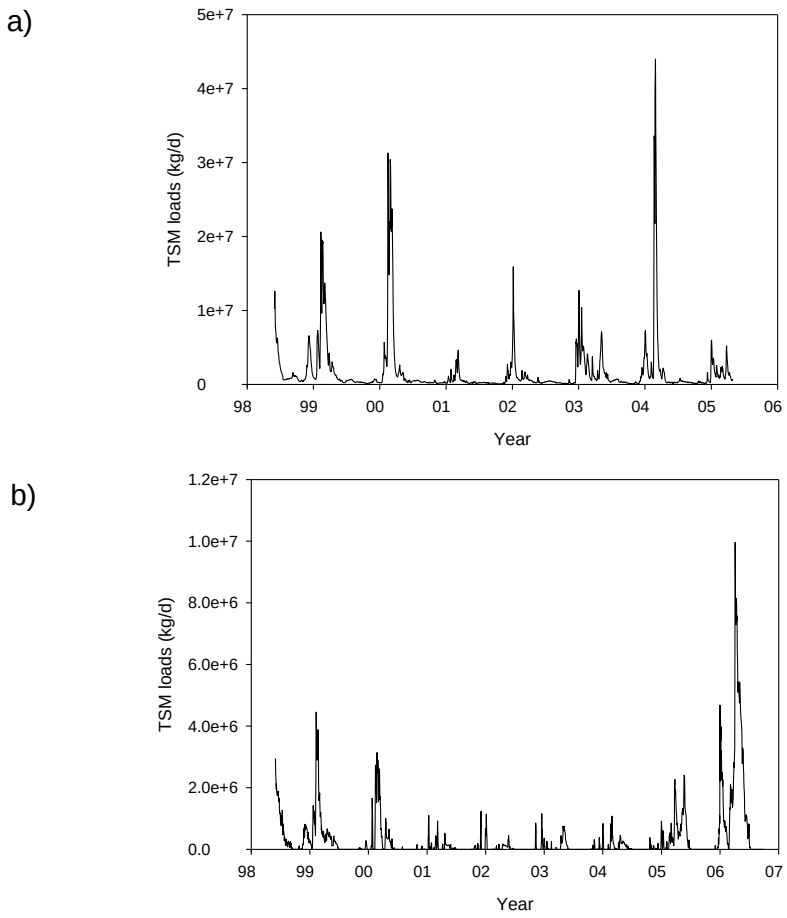


Figure 2-13 Model inputs of riverine loads of TSM for (a) Sacramento River at Rio Vista and (b) San Joaquin River at confluence (Data source: USGS). Note that y-axis values of TSM loads are about an order of magnitude lower for San Joaquin River compared to Sacramento River.

2.9.3 Phytoplankton

The riverine inputs of phytoplankton were specified as flow multiplied by time series chlorophyll a concentration data, for inputs from the Sacramento and San Joaquin Rivers. For the principal riverine input on Sacramento River at Rio Vista, data were reported on roughly a monthly basis. Data were obtained from the Bay Delta and Tributaries (BDAT) project site (http://bdat.ca.gov/index.html) and the USGS for the Sacramento River at Rio Vista as shown in Figure 2-14. Chlorophyll a concentrations were relatively high during 2002-2004. Riverine loads of phytoplankton from Sacramento River at Rio Vista are shown in Figure 2-15. Chlorophyll a concentration data from San Joaquin River at Twitchell Island obtained from BDAT multiplied by flow were used as San Joaquin River input (Figure 2-14). Inputs from the San Joaquin River were added as a point source at a location of X = 19,000m.

The seawater concentration was set at 2.3 μg Chl a/L as suggested in data from Cutter and Cutter (2004).

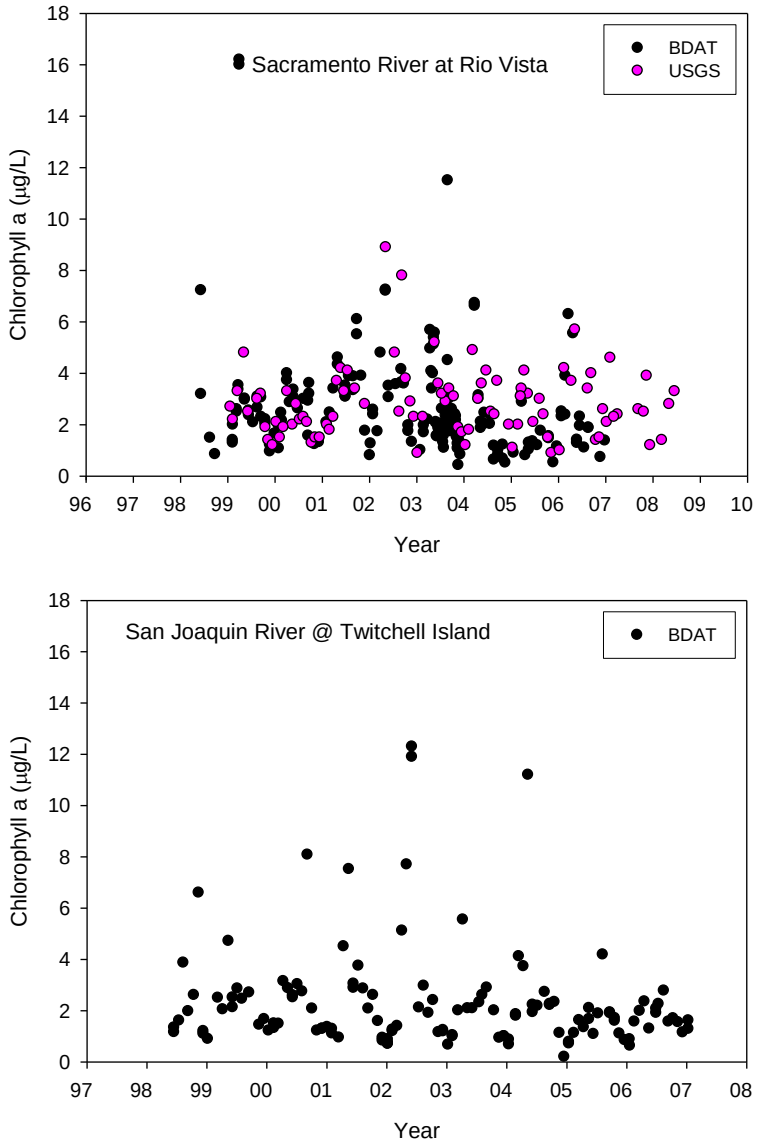


Figure 2-14 **Chlorophyll a concentrations at the head of the estuary in the Sacramento River at Rio Vista and in San Joaquin River at Twitchell Island (Data source: BDAT, USGS).**

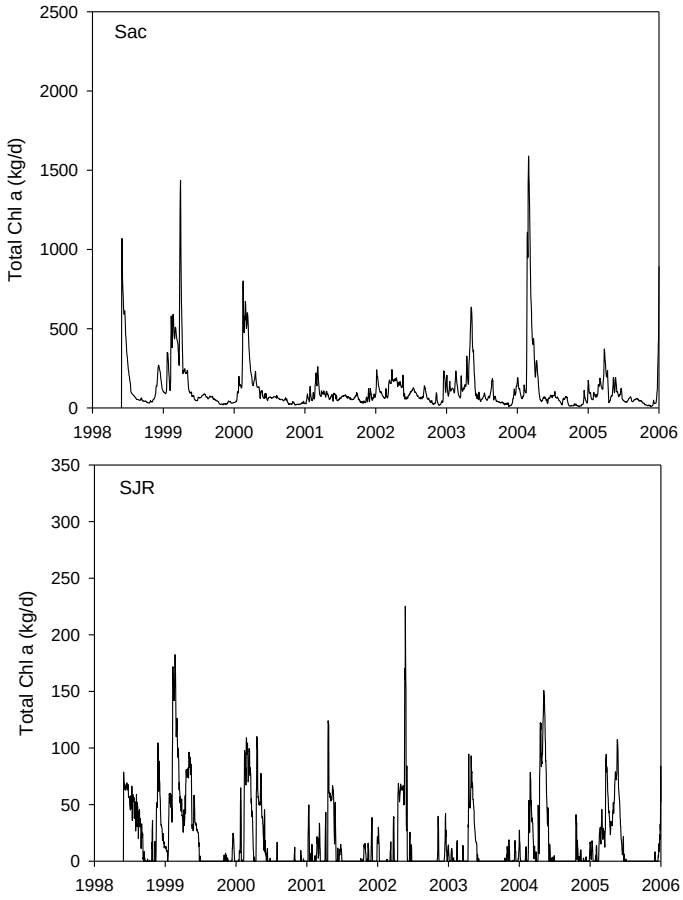


Figure 2-15 Riverine chlorophyll a loads at the head of the estuary in the Sacramento River at Rio Vista and San Joaquin River at confluence (Data source: BDAT, USGS).

2.9.4 Dissolved Selenium

The seawater end member of dissolved selenium was set at 1 nmol/L or 0.0789 µg/L (Cutter and Bruland, 1984).

Dissolved selenium inputs for selenate, selenite, and organic selenide were specified from the rivers as follows:

- **Sacramento River**: Selenium concentrations for each species from Sacramento River at Rio Vista multiplied by flow at Rio Vista.
- **San Joaquin River**: Selenium concentrations from San Joaquin River at Vernalis reduced by species-specific Delta removal constants, multiplied by flow from San Joaquin River at confluence (Figure 2-8). The Delta removal constants reflect loss of selenium in the Delta and export through aqueducts. The removal constants are parameters that are derived through the model calibration and were 0.74 for selenate, 0.67 for selenite, and 0.47 for selenide. Inputs from the San Joaquin River were added to the model at a location of X = 19 km. The approach used to define the input concentrations in the model are shown in Figure 2-16.

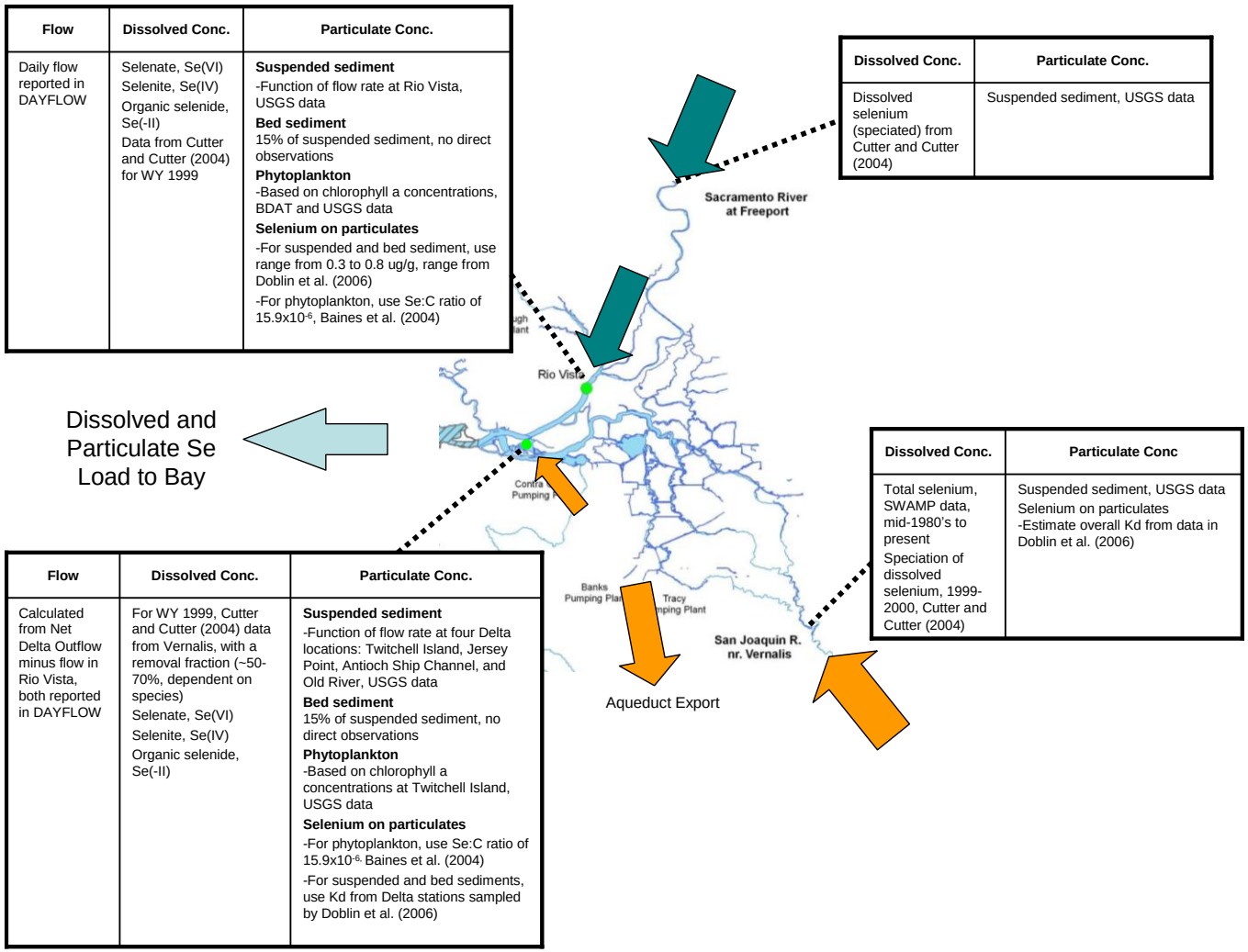


Figure 2-16 **Concentrations of selenium, dissolved and particulate, by species, for the Sacramento and San Joaquin Rivers. Flows measured or estimated at related locations (Freeport, Rio Vista, Vernalis, and the confluence of San Joaquin River with Sacramento River) are used to estimate loads that define the upper boundary of the model at Rio Vista. Selenium from San Joaquin River is added as a load (flow times concentration, by species) 19 km downstream of Rio Vista. The entire load from Vernalis does not reach the Bay because of uptake/settling in the Delta, as well as because of water export through the aqueducts.**

Concentrations of different species of dissolved selenium from Sacramento River at Freeport and San Joaquin River at Vernalis were simulated using the following general fitting equation, to account for dates for which measurements are not available:

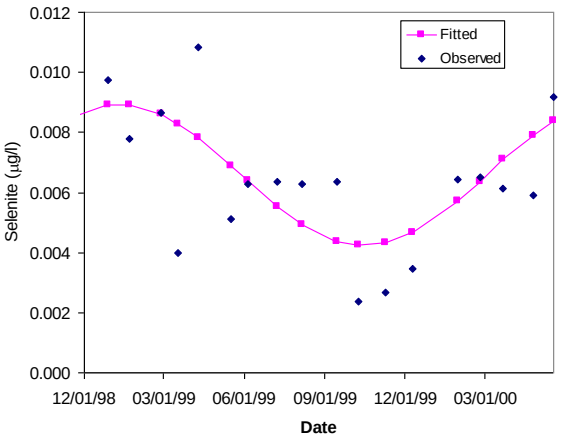
$$y = y_o + a_o * \sin\left(\frac{2*\pi*T}{b_o} + c_o\right) \quad (35)$$

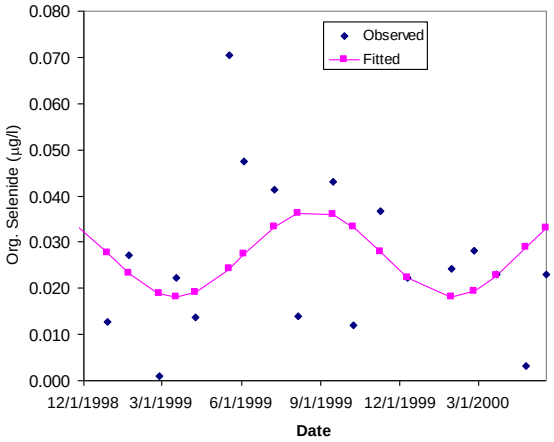
where y_o is the initial selenium concentration (µg/L) at when T = 0, a_o (µg/L), b_o, and c_o are fitting constants, π is the constant 3.1416, and T is the time in Julian days. Parameters for y_o, a_o, b_o, and c_o for three dissolved selenium species were derived based on measured concentrations at Sacramento River at Rio Vista and San Joaquin River at Vernalis as listed in Table 2-8. Selenium concentrations measured in the rivers are mainly for the year of 1998-2000. Measured and fitted concentrations for different species of selenium are shown in Figure 2-17 and Figure 2-18. The best fit parameters from the data were used to extrapolate concentrations for the simulation period of 1999-2006. These were multiplied by flow to estimate loads. Estimated daily dissolved selenium loads from the Sacramento River (at Rio Vista) and San Joaquin River (at the confluence) by different species are shown in Figure 2-19.

In a previous memo (TM2, Tetra Tech, 2008a), the relative contribution of dissolved selenium loads to the Bay from the Sacramento River and San Joaquin River was estimated using a slightly different set of assumptions. The TM-2 method used daily flow and monthly concentrations at Freeport to estimate loads from the Sacramento River. The San Joaquin River loads were estimated as daily flow multiplied by daily concentrations derived from a flow-concentration relationship at Vernalis and a delta removal constant of 0.6, as in Meseck (2002). Estimated annual dissolved selenium loads from the two rivers using these two methods (TM2 and the current model application) are similar (Figure 2-20), except for 2006 which was a very wet year. For the Sacramento River, the model used selenium concentrations at Freeport multiplied by flow at Rio Vista. This results in similar estimates of selenium loads from Sacramento River to the TM-2 estimates. For the San Joaquin River, the model used selenium concentrations at Vernalis multiplied by flow at the confluence and a calibrated removal constant (species-specific, listed in Table 3-3). The estimated loads used in the model are slightly lower than TM-2 estimates for dry years, although broadly comparable.

Table 2-8
Constants for Simulating Species of Dissolved Selenium for the Sacramento and San Joaquin River (after Meseck, 2002)

	a_o (µg/L)	b_o	c_o	yo (µg/L)	r
Sacramento River					
Selenite	0.016	75	0.41	0.022	0.69
Selenate	0.132	1556	3.77	0.503	0.44
Organic selenide	0.111	312	1.32	0.217	0.13
San Joaquin River					
Selenite	0.002	125	4.87	0.007	0.62
Selenate	0.023	622	5.30	0.047	0.57
Organic selenide	0.009	76	5.49	0.027	0.69





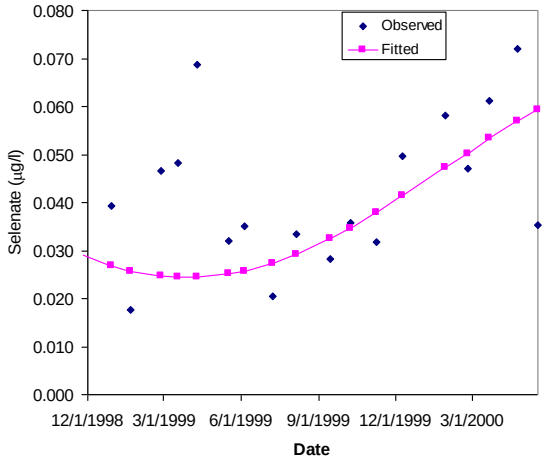


Figure 2-17 **Fitted dissolved selenium concentrations compared to observed concentrations from the Sacramento River at Rio Vista (Data source: Cutter and Cutter, 2004).**

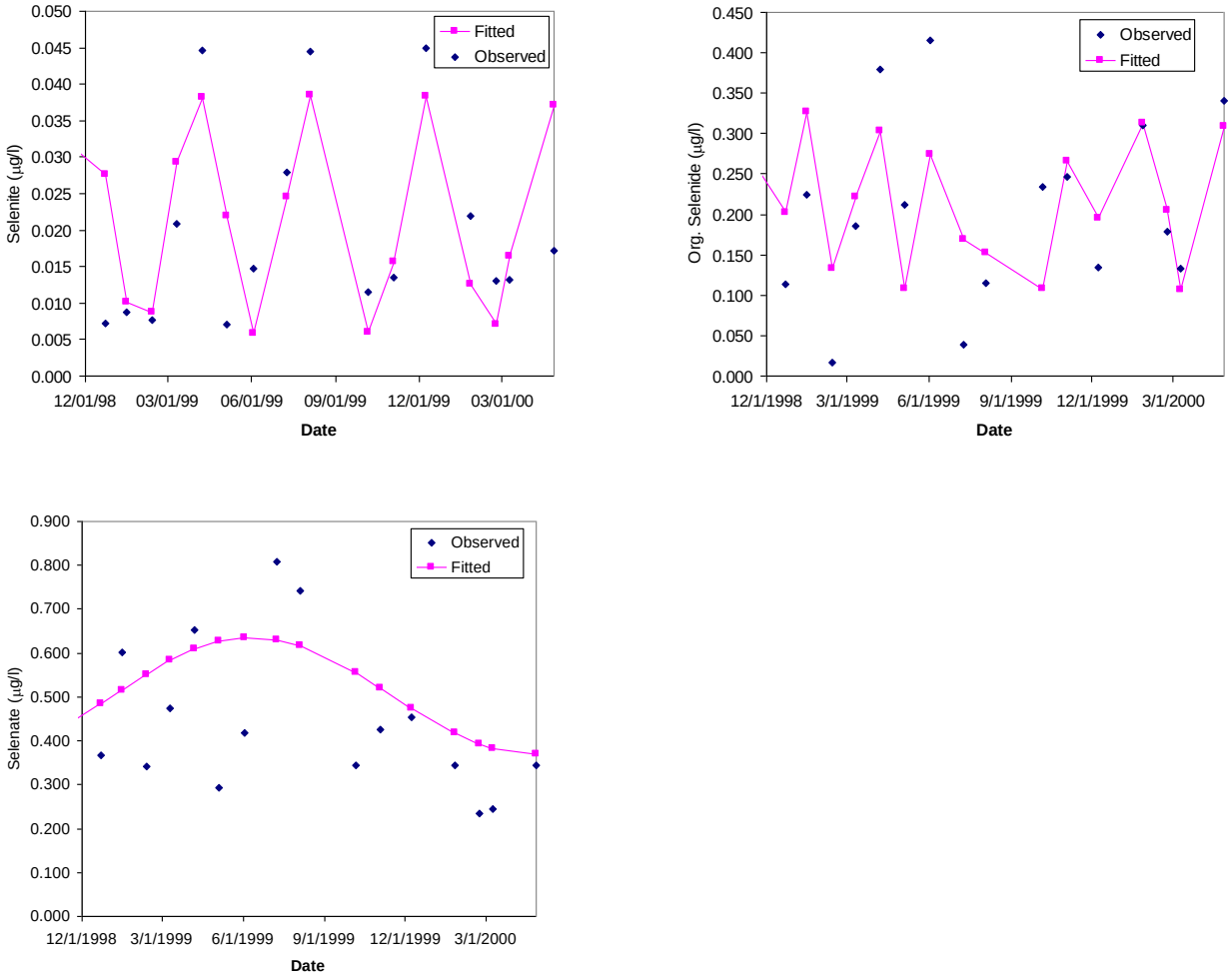


Figure 2-18 **Fitted dissolved selenium concentrations compared to observed concentrations from the San Joaquin River at Vernalis (Data source: Cutter and Cutter, 2004).**

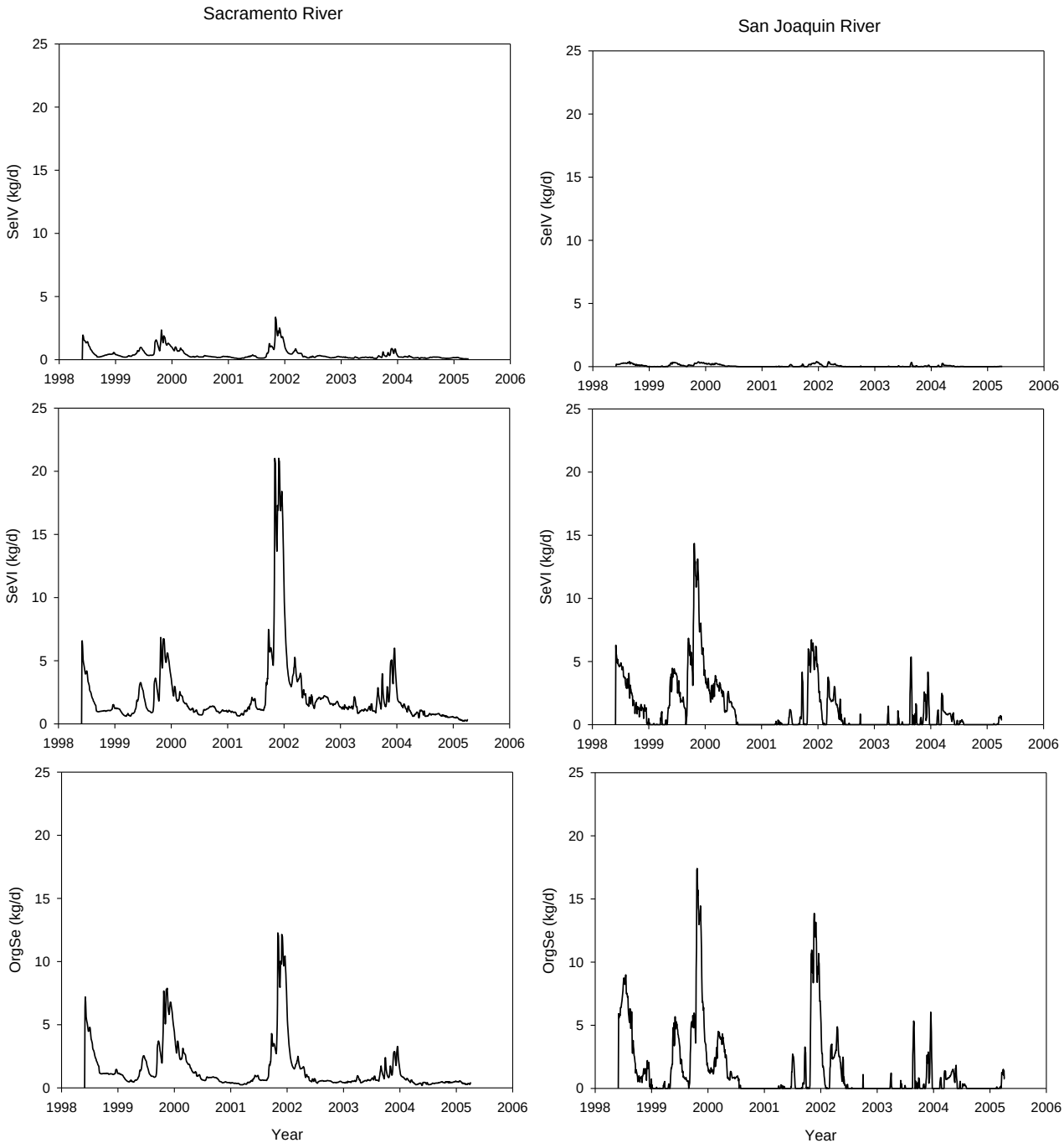


Figure 2-19 **Riverine inputs of different species of dissolved selenium from the Sacramento River at Rio Vista and the San Joaquin River at the confluence. Selenium concentrations underlying these load estimates were mainly for the years 1998-2000 and 1984-1988. During the 20 year period, selenium concentrations from the Sacramento River remain relatively constant (Cutter and Cutter, 2004).**

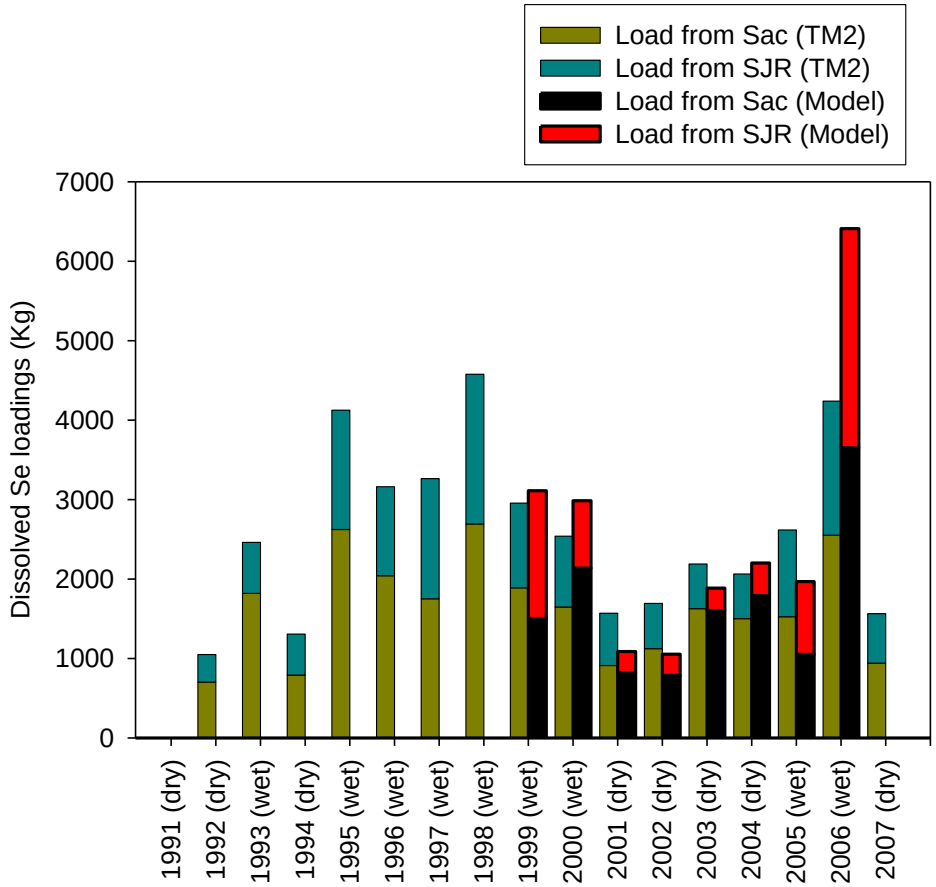


Figure 2-20 **Dissolved selenium loads from Sacramento River and San Joaquin River to the Bay estimated in TM2 and in the model (the load estimates were based on concentrations between 1998-2000).**

Daily selenium loads from local tributaries estimated in a previous technical memo by Tetra Tech (Tetra Tech, 2008a) were added to the model using the annual load for each hydrological area multiplied by a time series scaling factor, derived from daily flow record at Napa River (USGS11458000; Figure 2-21). No speciation data exist for local tributaries. The speciation from local tributaries is assumed to be the same as from the Sacramento River reported by Cutter and Cutter (2004): selenite (9%), organic selenide (35%) and selenate (56%). The total selenium load from tributaries estimated in the model varies depending on the volume of runoff each year, and was 819.7 kg/yr for 1999.

Daily refinery loads over 1999-2006 from five refineries in the NSFB estimated in Tetra Tech (2008a) were used in the model calibration, with speciation held constant at values reported by Cutter and Cutter (2004): selenite (13%), organic selenide (30%) and selenate (57%). The daily loads varied from day to day depending on the effluent data reported, and was 558.8 kg/yr for 1999.

A time series of refinery and tributary selenium loads is shown in Figure 2-22. The tributary loads were significant during the high flow season and minimal during the remainder of the year. Refinery loads are relatively constant throughout the year.

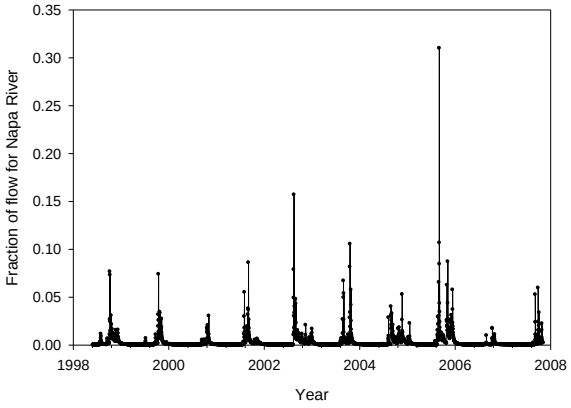


Figure 2-21 Flow as a fraction of mean annual flow at Napa River

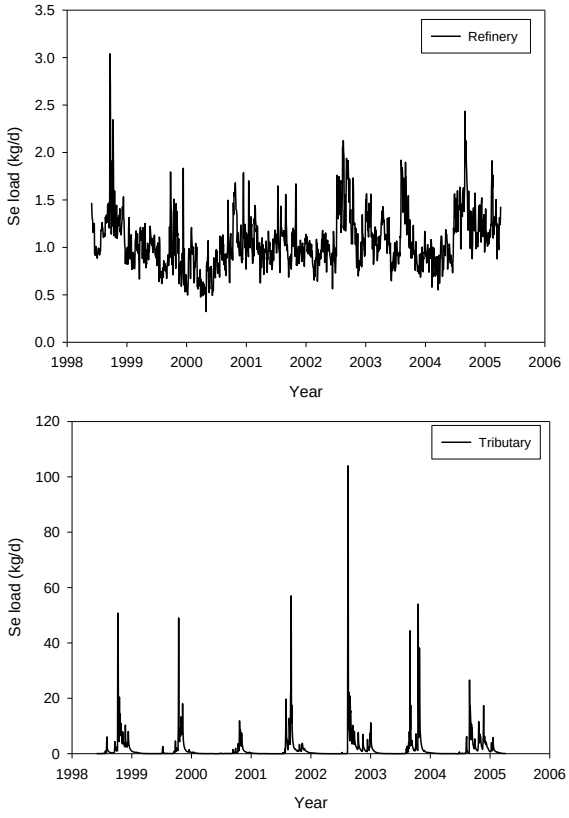


Figure 2-22 Daily refinery and tributary inputs of dissolved selenium

Selenium loads from other point sources including municipal and industrial wastewater discharges were also added to the model (Table 2-9). Speciation for municipal wastewater discharges used is organic selenide (15%), selenite (25%), and selenate (60%). The locations where selenium loads from point sources and tributaries were added to the estuary are also listed in Table 2-9. For these sources, the loading was specified as an average daily value for the entire period of the simulation because there was insufficient data from all dischargers to estimate load variability over 1999-2006. For 1999, the total loads from these POTWs sources were 175.8 kg/yr.

Table 2-9
Selenium Loads from Point Sources and Tributaries

Number	Point Source Name	Type	Distance from Head (km)	Daily Load (kg/d)
1	San Rafael	Tributary	80.9	0.207*
2	Berkeley	Tributary	87.9	0.103*
3	San Francisco Bayside	Tributary	95.1	0.037*
4	Novato	Tributary	70.9	0.155*
5	Petaluma River	Tributary	68.9	0.177*
6	Sonoma Creek	Tributary	65.5	0.188*
7	Napa River	Tributary	55.1	0.530*
8	Pinole	Tributary	72.6	0.127*
9	Fairfield	Tributary	36.8	0.367*
10	Concord	Tributary	41.2	0.407*
11	Tesoro	Refinery	42.1	0.19
12	Valero	Refinery	44.1	0.2
13	Shell	Refinery	45.9	0.59
14	ConocoPhillips	Refinery	59.2	0.16
15	Chevron	Refinery	76.8	0.33
16	City of American Canyon	Municipal	56.0	0.008
17	City of Benicia	Municipal	46.8	0.010
18	Central Contra Costa	Municipal	41.1	0.060
19	Central Marin	Municipal	8.0	0.034
20	Delta Diablo	Municipal	19.3	0.177
21	EBMUD	Municipal	98.9	0.095
22	Fairfield Suisun Sewer	Municipal	37.8	0.052
23	Las Gallinas	Municipal	74.0	0.009
24	Mount View	Municipal	44.3	0.006
25	Napa S.D.	Municipal	56.0	0.011
26	City of Petaluma	Municipal	71.6	0.019
27	Cities of Pinole and Hercules	Municipal	58.4	0.011
28	Rodeo	Municipal	59.0	0.002
29	Sausalito-Marin	Municipal	95.4	0.015
30	US Navy Treasure Island	Municipal	96.0	0.001
31	Vallejo Sanitation	Municipal	54.5	0.056
32	West County Agency WCA	Municipal	84.9	0.092
33	Rhodia Basic Chemical	Industrial	43.5	0.004
34	Dow Chemical	Industrial	20.7	0.006
35	General Chemical	Industrial	29.7	0.005
36	GWF (I)	Industrial	26.1	0.001
37	GWF (V)	Industrial	31.9	0.0004
38	USS-Posco	Industrial	20.1	0.031

*tributary loads are highly variable; the loads shown are mean daily loads.

Box 4. San Joaquin River Concentrations and Loads at Vernalis

The selenium loads from the San Joaquin River enter the Delta at Vernalis and are used as an input to the model. The Vernalis concentrations are attenuated by a removal constant before delivery to the NSFB, reflecting transformation/settling processes, as well as export in the aqueducts. Total selenium concentrations at Vernalis have been monitored at a relatively high frequency for more than two decades through the State of California's SWAMP monitoring program, and show a decline from values in the 1980s (Figure A below). Also, as discussed in the text, speciation data on selenium at Vernalis in 1999 have been reported by Cutter and Cutter (2004).

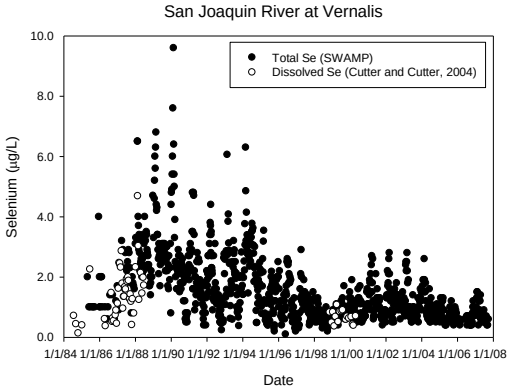


Figure A: Selenium data from Vernalis. The Cutter and Cutter (2004) data are for dissolved selenium, and the SWAMP data are for total (dissolved plus particulate) selenium.

For the model input, the speciated data for 1999, fitted with the trigonometric functions described in the text, was used to extrapolate concentrations over 1999-2006 in Vernalis. These concentrations were multiplied by the Delta removal constant for each species, and multiplied by flow at the San Joaquin river confluence to compute loads by species.

An alternative approach would be to use the total selenium data from SWAMP over 1999-2006, the ratios of selenium species from the Cutter and Cutter (2004) work, and the Delta removal constants to calculate loads delivered to the bay. The load estimation using the two approaches is compared in Figure B. For most years of the simulation, the two load estimation methods compare well. An exception is for 2006, which is a high flow year, where the SWAMP data approach resulted in a larger load estimate than the Cutter and Cutter (2004) data approach.

For model simulations over 1999-2006 presented in this work the Cutter and Cutter (2004) data-derived loads are used because of the speciation information. However, for simulations in years preceding 1999, the SWAMP data may be used.

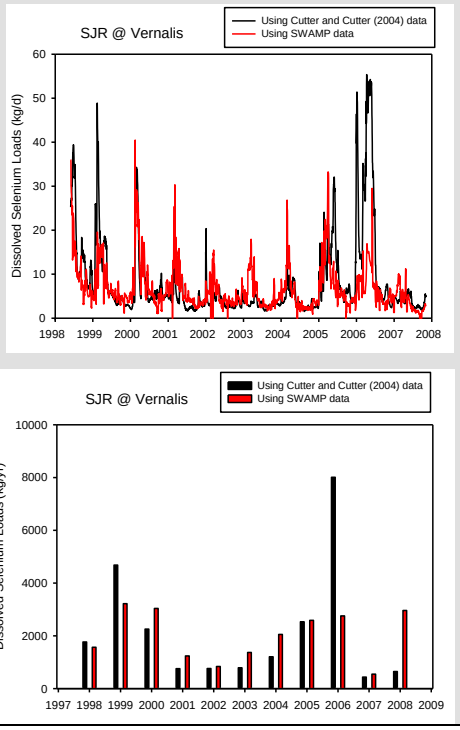


Figure B: Estimated selenium loads on a daily and a water year basis at Vernalis, computed using the Cutter and Cutter (2004) data and using the SWAMP data.

2.9.5 Particulate Selenium

Riverine particulate selenium inputs are estimated as selenium concentrations associated with PSP and BEPS (in µg/g), multiplied by riverine inputs of PSP and BEPS (in mg/l). Also added are the phytoplankton Se loads using a Se:C ratio and chlorophyll concentrations. The data sources used to define these inputs are shown in Figure 2-16. Box 5 explains the role of the Delta in particulate selenium transport.

Particulate selenium concentrations associated with PSP were previously reported by Doblin et al. (2006) and showed a range of values. Particulate selenium concentrations from riverine end members are 0.615 ± 0.205 µg/g at the Sacramento River and 0.655 ± 0.410 µg/g at the San Joaquin River (Doblin et al. 2006). Particulate elemental selenium ranged from 0.08-0.40 µg/g (0.149 ± 0.108 µg/g), particulate selenite and selenate range from non-detectable to 0.25 µg/g (0.270 ± 0.137 µg/g), and organic selenide concentrations ranged from 0.015-0.74 µg/g (0.134 ± 0.238 µg/g) at Sacramento River at Rio Vista (Doblin et al. 2006). Particulate selenium measured at this location by Doblin et al. (2006) may possibly be influenced by the bay, particularly during low flow. During high flow, particulate selenium at this location may better reflect input from the Sacramento River. Concentrations associated with PSP at the head of the estuary (Rio Vista) are calibrated parameters. Once calibrated, selenium concentrations on particulates were kept constant through the simulation period of 1999-2006.

Particulate selenium loads from the San Joaquin River were estimated based on TSP loads and estimated particulate selenium concentrations from dissolved selenium concentrations (using species-specific K_d values derived based on data from the Delta, Appendix 4) for San Joaquin River at the confluence. If the San Joaquin River has higher particulate selenium concentrations, then mixing with Sacramento River and bay water may lower the concentrations. Data on particulate selenium further upstream would needed to more directly estimate this particulate source, and no such data have been reported. However, from the standpoint of the model representation here, the San Joaquin River enters the bay through the Delta, and the effects of the Delta on the particulate selenium cannot be neglected. Particulate selenium concentrations have not been measured in San Joaquin River upstream from the Delta, yet, the river forms a conduit for transporting potentially large loads of particulate selenium from Central Valley to the Bay. The magnitude of the particulate load and the impact of the Delta on delivery of this load to the Bay need further studies/considerations.

Seawater endmember concentrations of PSP associated particulate selenium can be derived from model calibration, or observed concentrations at the Central Bay by Doblin et al. (2006) can be used. For the calibration presented here, a value of 1.22 µg/g was used as the seawater boundary condition, based on calibration. Because the seawater boundary condition is somewhat poorly defined, calculations were also presented with a range of boundary conditions from 0.96 to 1.22 µg/g, as discussed in Section 4.

Selenium concentrations in bed sediment were derived from Meseck (2002) along the longitude of the estuary as shown in Table 2-11 (at distance = 0). Seawater endmember concentrations of BEPS-associated particulate selenium were specified as 0.

Particulate selenium associated with phytoplankton is assumed to have a riverine boundary concentration of 15.9 μg Se/ g C (Baines et al. 2004). The observed time-series data of chlorophyll a concentrations at Rio Vista and a C: Chl a ratio of 51 were used to estimate particulate selenium inputs associated with phytoplankton. The C:Chl a ratio of 51 was derived from Alpine and Cloern (1992) and used as the Delta input. This value was based on an average of the carbon:Chl a uptake ratio in the bay. C:Chl a ratios vary with phytoplankton species and growth phase, and a wide range of values has been reported in the literature (e.g., 10 to > 300, reviewed by Cloern et al., 1995; and 27-67 by Riemann et al., 1989). Variation of chlorophyll a content in phytoplankton in space and time was beyond the scope of this application and the Alpine and Cloern (1991) value was used throughout the calculation. The seawater end member of particulate selenium associated with phytoplankton is specified at 21.0 μg Se/g C. This number is in the range of the particulate selenium concentrations in phytoplankton found in the North San Francisco Bay, listed in Table 2-2.

Particulate selenium concentrations from different endmembers including the bed sediments, water column, riverine inputs from Sacramento at Rio Vista, San Joaquin River, Golden Gate, and phytoplankton are shown in Figure 2-23. The particulate selenium concentrations in the water column are closest to concentrations from Rio Vista and the Golden Gate, and were higher than concentrations in bed sediments. This suggests the influence from bed sediments on seston particulate selenium is not as significant as expected in other estuaries. Although the contribution may be small, the process of interaction with bed sediments is simulated by the model.

Table 2-10
Selenium Concentrations Sssociated with PSP Used in the Model for Sacramento River at Rio Vista (after Meseck, 2002)

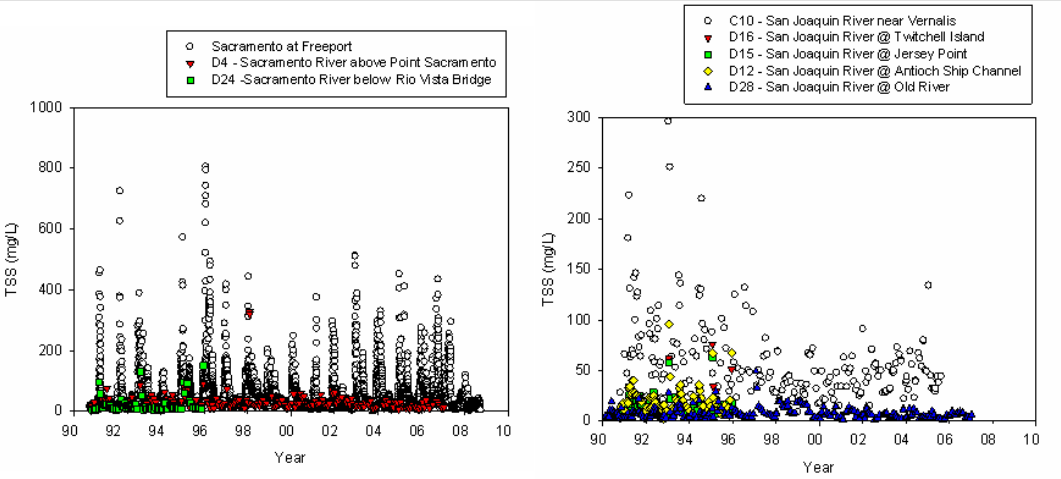
	Elemental Selenium in PSP (μg/g)	Selenate and Selenite in PSP (μg/g)	Org. Selenide in PSP (μg/g)
Mean	0.270	0.149	0.134
Standard Deviation	0.137	0.108	0.238
Range	N.D. to 0.25	0.08 – 0.4	0.015 – 0.74

Table 2-11
Selenium Concentrations Sssociated with BEPS used in the Model (after Meseck, 2002)

Distance from Sacramento at Rio Vista (km)	Elemental Selenium in BEPS (μg/g)	Selenate and Selenite in BEPS (μg/g)	Org. Selenide in BEPS (μg/g)
0.0	0.123	0.052	0.079
15.0	0.123	0.052	0.079
25.4	0.109	0.058	0.120
27.5	0.110	0.047	0.070
41.6	0.099	0.045	0.072
53.0	0.118	0.061	0.092
66.2	0.099	0.052	0.080

Box 5. TSS Transport through the Delta

Characterization of the total suspended sediment (TSS) loads from the Delta, and the associated particulate selenium, is an important model input, and was estimated using measured TSS concentrations, and estimates of selenium content. For the model, the inputs that are used directly include the values entering the simulated portion of the estuary, beginning at Rio Vista. San Joaquin inputs are introduced 19 km downstream near the confluence of the two rivers. However, it is important to understand that TSS loads are significantly attenuated by transport through the Delta as shown below. Open circles show values at the locations where the rivers enter the Delta (Freeport and Vernalis), and the colored symbols show concentrations at various Delta locations. Because of the reduction in TSS, selenium associated with particulates is also similarly attenuated, and the loads entering the bay are smaller than the loads entering the Delta.



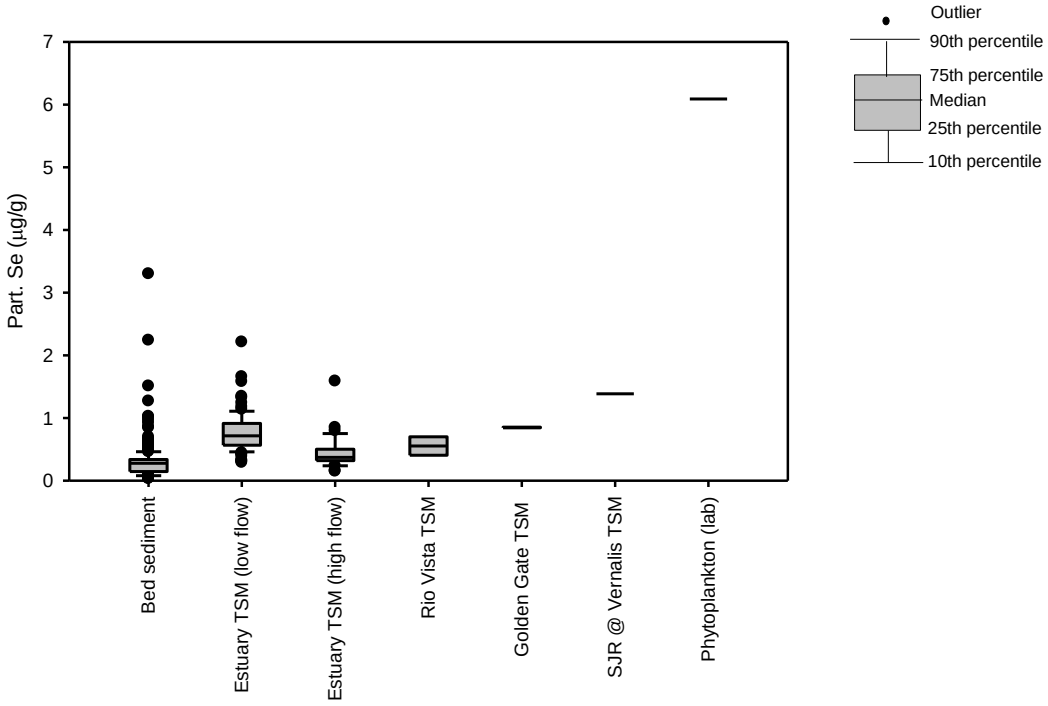


Figure 2-23 Observed particulate selenium concentrations from different endmembers (Source: RMP, Doblin et al. 2006).

Particulate selenium loads from the Delta were previously estimated using annual TSS loads from the Delta estimated by McKee et al. (2006) and selenium concentrations on particulates from Doblin et al. (2006) (Tetra Tech 2008a). McKee et al. (2006) estimated TSS loads from the Delta based on measurements at Mallard Island and accounted for both advective and dispersive fluxes. In this model application, as noted above, riverine inputs of particulate selenium are estimated as PSP and BEPS loads multiplied by selenium concentrations on particulates. The two methods yield similar annual particulate selenium loads to the Bay (Figure 2-19). Estimated particulate selenium loads from the Sacramento River at Rio Vista are greater than the San Joaquin River (Figure 2-24). Particulate selenium loads from the Sacramento River at Freeport and San Joaquin River are Vernalis are greater than the loads entering the Bay due to deposition in the Delta (Figure 2-25).

Particulate selenium loads from POTWs, refineries and tributaries are assumed to be zero.

South San Francisco Bay selenium loads into the Central Bay were also estimated for the model, although model testing showed that concentrations in NSFB were relatively insensitive to loads from the South Bay. The load was based primarily on contributions from the Guadalupe River because of high observed selenium concentrations. Flow from the Guadalupe River ranges from 35.63 Mm^3/yr to 126.73 Mm^3/yr. Average selenium concentrations in the Guadalupe River were 4.76 µg/L (Tetra Tech, 2008a). The estimated selenium loads that enter the South Bay range from 169.6-603.2 kg/yr. Speciation data are not available for the South Bay for recent years. The loads were assumed to be in dominantly in the selenate form and not retained significantly in South Bay. Given the insensitivity of the NSFB concentrations to South Bay loads, the load was not varied from year to year, and a median value 365 kg/yr of selenium load (as selenate) from South Bay was used for all years of the simulation. No particulate selenium contribution from the South Bay was assumed.

2.10. SUMMARY OF MODELING APPROACH

Although complex, the approach presented here makes the best available use of existing information in NSFB that influences selenium loads, transformations and biological uptake. To the extent feasible the inputs are derived for a time frame spanning 1999-2006. Over this time, relatively complete data records were available for flows, chlorophyll a, suspended sediments, and salinity.

For total selenium, all known inputs relating to riverine sources, point sources, and local tributaries have been represented in this work. There were generally good data records for most point sources, including refineries, POTWs, and the San Joaquin River. Not all total selenium data were fully defined over the entire period 1999-2006, and two approaches were used to fill in the gaps. For riverine loads for the Sacramento and San Joaquin Rivers and for the local tributaries to the bay, relationships were developed between flows and concentrations, and these relationships were used to estimate concentrations, and thus loads, for dates during which selenium measurements were not available. For point sources, where daily data were not available for the entire period, primarily POTWs and non-refinery industrial discharges, an average daily load was computed, and was applied over the entire period of the simulation.

In contrast to total selenium data, speciation information relating to the sources was only available for a limited number of dates ending in 1999. Speciation of source loads for other years was largely based on data from 1999.

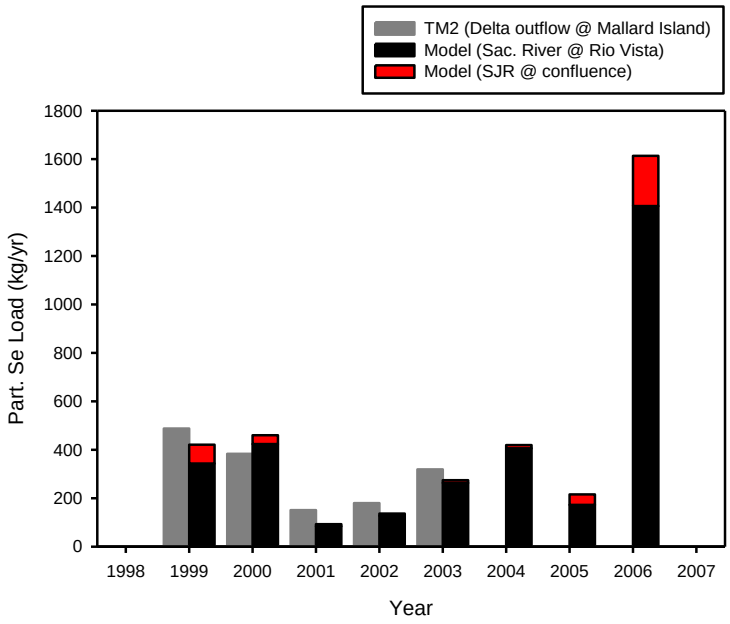


Figure 2-24 **Particulate selenium inputs to the Bay estimated in TM2 (Tetra Tech, 2008a) and in the model. The TM-2 load estimates were computed using measured suspended sediment outflow from the Delta, multiplied by the average selenium content on particles (0.64 µg/g). The approach used for the model was based on riverine flows, flow-TSS relationships, and partitioning between dissolved and particulate phases. For years during which both methods apply (1999-2003), the load estimates are similar.**

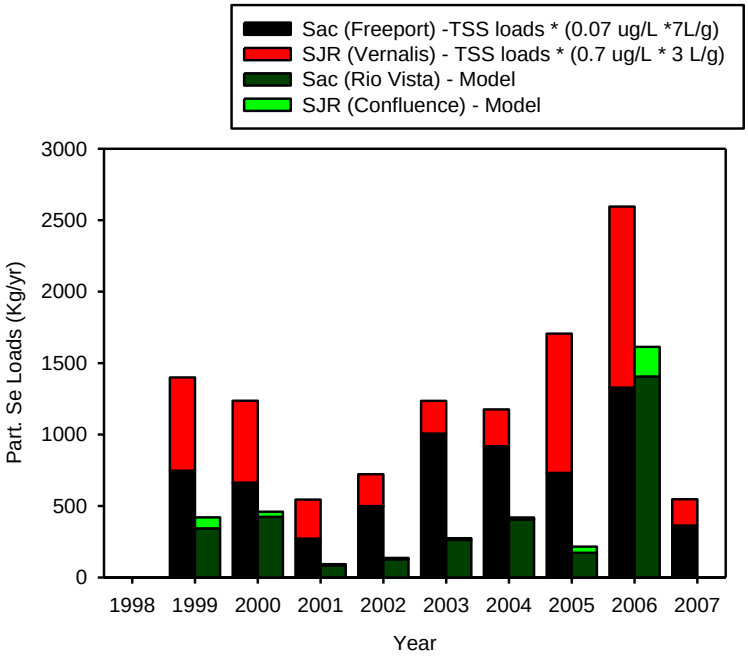


Figure 2-25 **Loads estimated upriver at Freeport (Sacramento River) and Vernalis (San Joaquin River) compared to model inputs of particulate selenium loads to the bay from the two rivers at Rio Vista (Sacramento River) and a point on the San Joaquin River near the confluence with the Sacramento River. Dissolved selenium concentrations and partitioning coefficients for Sacramento River at Freeport and San Joaquin River at Vernalis were data from Cutter and Cutter (2004) and Doblin et al. (2006) for 1998-2000. The estimates show a significant reduction of particulate selenium from the two rivers during transport through the Delta (also see Box 4).**

3. MODEL CALIBRATION AND EVALUATION

3.1. CALIBRATION PROCESS

The model calibration involved the selection of a variety of parameters to represent processed in NSFB. Some model parameters and inputs are poorly quantified given the available dataset or show a wide range, and calibration is needed to obtain the best fit of the model prediction to the observed values, whereas others are relatively well-quantified in the literature or available data. The latter include the bathymetry and total length of the estuary, parameters used to simulate tidal variation, flow from the rivers, and point-source loads. Meseck (2002) classified model parameters into three categories: well-known parameters, moderately known, and poorly known parameters (Table 3-1). Parameters obtained directly from the literature without fitting are listed in Table 3-2.

Because the model as generally formulated in Section 2, has previously been calibrated, (Meseck, 2002; and Meseck and Cutter, 2006), minimal changes were made to previously calibrated parameters. The parameters adjusted are constrained by values reported in the literature. Parameter values that were derived through calibration were generally moderately or poorly known parameters, as listed in Table 3-3.

Table 3-1
Classification of Parameters Needed in ECoS to Simulate the Biogeochemical Cycle of Selenium in NSFB (after Meseck, 2002)

Well-known Parameters	**In Equation**
River flow	(30)
Cross section area	
Refinery inputs	
Tidal amplitudes	(8)
Irradiance	
Initial salinity	
TSM	
Moderately-known Parameters	
P_m – maximum photosynthesis rate	(10)
α- slope of light saturation curve	(10)
r-respiration rate	(9)
W- zooplankton weight	(A1)
k_1-k_3 – dissolved selenium oxidation rate constants	(14-16)
Z – zooplankton abundance	
Selenium concentration in bottom sediment	(A2)
Poorly-known Parameters	
d, e, ε and ψ - scaling factors to simulate transport of bed exchanged particulate material	(4) (5)
ks – light attenuation coefficient	
k_4-k_6 – phytoplankton uptake rates of selenite, selenate, and organic selenide	(13)
Delta removal constant of selenium	(14-16)
Tributary loads	

Table 3-2
Parameter Values Derived from the Literature (after Meseck, 2002)

Parameter	Description	Value	Units	Reference
M_2 phase	Tidal phase	125	degrees	Godin (1972)
K_1 phase	Tidal phase	264	degrees	Godin (1972)
O_1 phase	Tidal phase	51	degrees	Godin (1972)
M_2 frequency	Tidal frequency	595.52	Degrees/d	Godin (1972)
K_1 frequency	Tidal frequency	360.96	Degrees/d	Godin (1972)
O_1 frequency	Tidal frequency	334.56	Degrees/d	Godin (1972)
M_2	Tidal amplitude	0.58	m	Uncles and Peterson (1996)
K_1	Tidal amplitude	0.37	m	Uncles and Peterson (1996)
O_1	Tidal amplitude	0.23	m	Uncles and Peterson (1996)
Vs	Sinking rate of BEPS	86.4	m/d	McDonald and Cheng (1997)
BEPSsea	Sea water end member of BEPS	0	g/d	Harris et al. (1984)
PSPsea	Sea water end member of PSP	0.01	g/L	Harris et al. (1984)
ws	Sinking rate of phytoplankton	0.5	d^{-1}	Lucas et al. (1998)
W	Zooplankton weight	13	mg C/animal	Hutchinson (1981)
Bsea	Initial phytoplankton concentrations and seawater end member	2.3	µg Chl-a/l	Alpine and Cloern (1992)
rphyto	Non-specific mortality	0.1	d^{-1}	Cole and Cloern (1994)
C:Chl a	Carbon to Chl a ratio	51	mg C/mg Chl a	Alpine and Cloern (1992)
k_3	Rate constant, SeIV-> SeVI	2.4×10^{-6}	d^{-1}	Cutter and Bruland (1984)
k_4	Uptake rate of SeIV by phytoplankton	15.78 0.00076	1/(g Chl a)/hr l/day (under chl a = 2 µg/L)	Riedel et al. (1996)
k_5	Uptake rate of SeVI by phytoplankton	3.37 0.00016	1/(g Chl a)/hr l/day (under chl a = 2 µg/L)	Riedel et al. (1996)
k_6	Uptake rate of Org Se-II by phytoplankton	7.89 0.00038	1/(g Chl a)/hr 1/day (under chl a = 2 µg/L)	Riedel et al. (1996)
Z	Zooplankton abundance	30-230	Animal/L	Pukerson et al. (2003)
Phyto Se:C river	Phytoplankton Se in the river	15.9	Ratio	Baines et al. (2004)
Phyto Se:C sea	Phytoplankton Se in seawater	23.9	Ratio	Doblin et al. (2006)

Table 3-3
Parameter Values Derived Through Model Calibration

Parameter	Description	Value	Standard Deviation	95% Confidence Interval	Units	Literature Range	Reference
kw	Dispersion coefficient	362	± 16	362 ± 7.7	m/s^2	16-812	Cifuentes (1990)
a	Resuspended sediment at river end member	0.0046			g/L		Calibration
b	Permanently suspended sediment at the riverine end	0.00029			g/L		Calibration
c	Scales freshwater discharge to sediment input	0.7					Calibration
d	Scaling factor for Ubeps	0.322					Calibration
e	Scaling factor for Ubeps	793					Calibration
ε	Scaling factor for Kbeps	1.99			m		Calibration
ψ	Scaling factor for Kbeps	3.2e6			m		Calibration
P_m	Maximum rate of photosynthesis	100.6	± 1.50	100.6 ± 0.72	mg C/mg Chl-a/d	24-219	Alpine and Cloern (1992)
α	Slope of light-saturation curve divided by Pm	0.00397			$Einst.m^2/d$	0.002-0.009	Peterson and Festa (1984)
Pb	Benthic grazing rate	0.037	± 0.002	0.037 ± 0.001	d^{-1}		
k_1	Rate constant, pSe-II -> d org Se-II	0.0066			d^{-1}	1.3×10^{-5}- 5×10^{-2}	Cutter (1992)
k_2	Rate constant, d org Se-II -> SeIV	0.004			d^{-1}	1.0×10^{-3} – 81.0	Cutter (1992)
Se OPSP	Elemental selenium in PSP at Rio Vista	0.100	± 0.034	0.100 ± 0.016	µg/g	0.08-0.40	Calibration; Doblin et al. (2006)
Se (IV+VI)PSP	Se IV+VI selenium in PSP at Rio Vista	0.202	± 0.016	0.202 ± 0.008	µg/g	0-0.25	Calibration; Doblin et al. (2006)
Org. Se-II PSP	Org. Se-II selenium in PSP at Rio Vista	0.166	± 0.076	0.166 ± 0.076	µg/g	0.015-0.74	Calibration; Doblin et al. (2006)
Delta –San Joaquin River input constant (1- removal constant); dissolved species only	fSeVI	0.260	± 0.125	0.260 ± 0.060			Calibration
	fSeIV	0.326	± 0.232	0.326 ± 0.112			Calibration
	fSeII	0.534	± 0.342	0.534 ± 0.165			Calibration
a'	adsorption	0.0013			l/g/d	0.1-0.8	Zhang and Sparks (1990)
BEPSriver	Riverine end member of BEPS	0.00463			g/L		Harris et al. (1984)

Calibration of the model followed the sequence of fitting physical variables (salinity and TSM), followed by biological (e.g., phytoplankton) and chemical variables (dissolved and particulate selenium). The sequence selected is such that parameters calibrated in subsequent steps do not affect prior parameters. Thus, calibration of parameters related to phytoplankton will not change the parameters fitted for salinity. Likewise, parameters for selenium species will not have an effect on the salinity, phytoplankton, or TSM. The fitting process was as follows:

Step 1: Salinity (1 parameter)

Step 2: TSM (4 parameters)

Step 3: Phytoplankton (3 parameters)

Step 4: Dissolved selenium species (selenate, selenite, and selenide) (5 parameters, and the delta removal constants for each species)

Step 5: Particulate selenium (elemental selenium, selenite+selenate, selenide) (3 parameters)

The dataset used in calibrating the physical variables (salinity, TSM) and phytoplankton were obtained from the USGS (http://sfbay.wr.usgs.gov/access/wqdata/). The main calibration time periods for these parameters are roughly on monthly intervals from January 1999 to December 1999. Data used in calibration include 19 USGS monitoring stations located in the North Bay as shown in Figure 1-4. As discussed below, data for these constituents were measured at a higher frequency than the selenium data (typically every two months).

The model calibration for selenium was mainly performed using data from 1999. Water year 1999 has detailed selenium speciation data sampled during low and high flow periods. Water year 1999 also represents conditions for which detailed refinery discharge data are available. Further, refinery loads were decreased by about two-thirds in mid-1998, and have stayed at approximately those levels since that time. Thus, 1999 data represent post refinery-cleanup conditions, and are somewhat representative of more recent conditions. Importantly, no detailed speciation data on selenium are available after 1999.

For the application in the NSFB, the model was run on a time step of 1 day. The spin-up time for model simulation is approximately 180 days starting from June 1, 1998.

The model calibration was conducted based on a least squares minimization approach, using a fitting program provided by Dr. John Harris, the developer of the ECoS code (Harris, 2003). For each iteration, the sum of square deviation between observed and simulated values was calculated by the program and the parameters were adjusted for the next iteration to minimize the sum of square errors. Estimates of mean and standard deviation of the parameters calibrated and sum of squared deviation are provided by the program as calibration results. Example results are shown in Appendix 3.

The DYMBAM component of the model does not require model fitting, and was applied after the other physical, biological, and chemical variables were computed.

The model goodness of fit was evaluated using two measures: the correlation coefficient (r) between predicted and observed values, a goodness of fit defined in Perrin et al. (2001).

$$GOF(\%) = 100 * \left(1 - \left| \sqrt{\frac{\sum Xcal}{\sum Xobs}} - \sqrt{\frac{\sum Xobs}{\sum Xcal}} \right| \right) \quad (29)$$

where, Xcal is the model simulated concentration and Xobs is the observed concentration. A 100% goodness of fit indicates a perfect fit between simulated and observed values.

The dates selected for calibration of selenium speciation and transformation are April 13, 1999 (high flow) and November 11, 1999 (low flow), with available data from Cutter and Cutter (2004) and Doblin et al. (2006). Because selenium data were collected based on salinity intervals, locations of sample stations vary during low and high flow. For model calibration, station pairs for April and November that are in close proximity were lumped as one station and resulted in a total of 13 stations with two data points in time. The data pairs with dissolved selenium concentrations are shown in Figure 3-1. As shown in Figure 3-1, selenate concentrations were elevated in the middle of the estuary during low flow, corresponding to relatively higher point source inputs. For selenium, the calibration follows the sequence of selenate, organic selenide and selenite, particulate elemental selenium, particulate organic selenide and particulate adsorbed selenite. Organic selenide can be oxidized to selenite, therefore it can influence selenite and was calibrated first. Particulate selenium is influenced by dissolved selenium through phytoplankton uptake and adsorption and therefore was calibrated after dissolved selenium.

Although the sequence of parameter fitting employed here was selected such that parameters related to one constituent did not affect previously fitted parameters, multiple parameters/processes can affect one common constituent and there is no clear guidance on selecting a parameter to fit first. In principle, when there are multiple parameters in a single differential equation representing a constituent, it may be better to calibrate using multiple parameters simultaneously; however, calibrating multiple parameters at the same time sometimes resulted in negative or unrealistic values and resulted in significantly longer run times. Therefore, the final set of parameters presented here were based on calibration of one parameter at a time, performed in five sequential steps for each major class of constituent.

The following sections describe the calibration process of each parameter in the model.

3.1.1 Salinity

In ECoS, salinity is mostly determined by boundary conditions and hydrological forcings that affect mixing (river flow, tides). Inputs for simulating salinity are generally well quantified. The salinity is simulated as a result of advection and dispersion. Dispersion is simulated using a single dispersion coefficient (Kw), which reflects the result of mixing. Calibration for salinity mainly involves adjusting the dispersion coefficient Kw. In Meseck (2002), salinity was modeled as a dynamic function of salinity gradient and velocity, which may result in linear salinity profiles. Kw calibrated based on monthly observed salinity data in 1999 indicates dispersion coefficient varies across the year, but generally ranges between 254 – 538 m^2/s. However no relationship between Kw and flow was found. Therefore, for 1999, the estimated monthly Kw values were used in the model simulation. Kw values between sampling dates were linearly interpolated by the model. For time periods after 1999, Kw used is the calibrated value (362 m^2/s) based on all data in 1999. The calibrated Kw value using all data in 1999 results in relatively low standard deviation (Table 3-3).

3.1.2 TSM

Calibration for TSM involved adjusting parameters that determine location and shape of estuarine turbidity maximum (d, e, ε and ψ) and riverine boundary conditions that define concentrations at the head of the estuary. Riverine concentrations of TSM simulated using equation (27) compared well with observed TSM at Sacramento River at Rio Vista (12-42 mg/L observed vs. 20-45.6 mg/L simulated at the head of boundary).

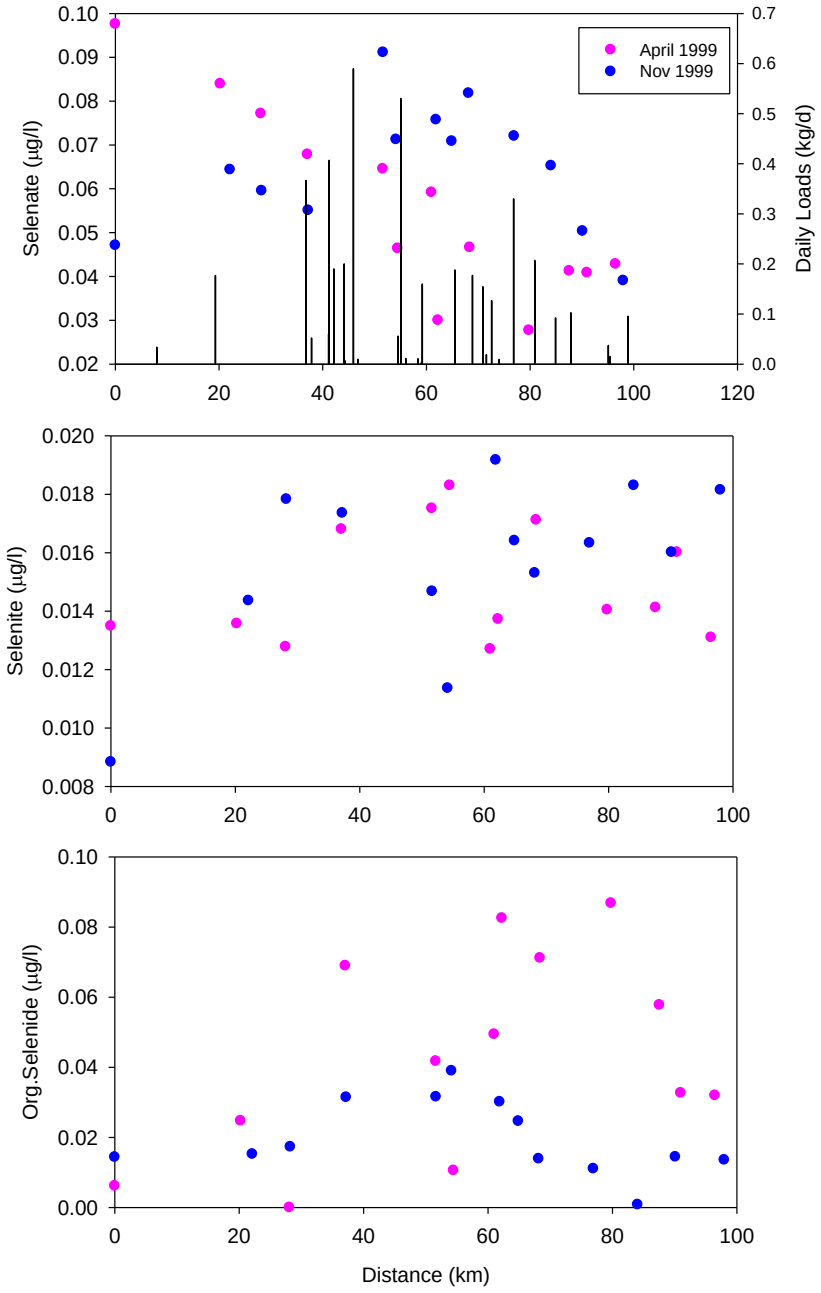


Figure 3-1 **Dissolved selenium concentrations for stations used in calibration, with mean daily loads from refineries, tributaries, and POTWs shown. Data points shown are individual values.**

3.1.3 Phytoplankton

Calibration of phytoplankton involved adjusting parameters related to zooplankton grazing. Spatial distribution of zooplankton abundance was derived from Pukerson et al. (2003). Grazing was assumed to occur during summer months between June-October, and was held at zero for most months for the rest of the year. The calibration involves varying the grazing rates across the grazing months. The other parameter calibrated is the maximum rate of photosynthesis (*Pm*). Estimated standard deviation for the calibrated Pm is small (Table 3-3).

3.1.4 Dissolved selenium

Concentrations of different species of dissolved selenium from riverine inputs are simulated using the same sine wave function as in Meseck (2002), with parameters listed in Table 2-8. A key parameter with significant uncertainty is the Delta load removal constant, which is adjusted to predict dissolved selenium concentrations. The calibrated San Joaquin River load constants (1 – removal constant; for convenience) range between 0.268 (selenate) – 0.558 (organic selenide) for different species. The calibrated load constants have relatively large standard deviation or coefficient of variance. The coefficients of variation are about 50% (0.446 – 0.557), suggesting the relatively large uncertainties in the San Joaquin River loads.

Selenite uptake rates by phytoplankton measured by Baines et al. (2004) at ambient selenite concentrations (0.29 nmol/l) similar to the observed selenite concentrations in the NSFB were first used. Uptake rates measured by Baines et al. (2004) in laboratory tests were 0.33 pmol Se/(μg Chl a)/hr. However, the uptake rates result in Se:C ratios much higher than observed values of 15.9 μg/g in the Delta. Therefore, lower uptake rates (normalized to ambient selenite concentrations), as in Riedel et al. (1996) and in Meseck and Cutter (2006) were used, and a more reasonable selenium content (measured as Se:C ratio) in phytoplankton is predicted. Uptake rates of selenate and organic selenide were at 25% and 50% of selenite, as suggested in previous experimental studies (Riedel et al., 1996; Baines et al., 2001). Increasing organic selenite uptake rate to same as selenite did not result in significant changes in particulate organic selenide. This may be due to both low organic selenide concentration in the estuary and, even with the increase, relatively low uptake.

3.1.5 Particulate selenium

For particulate selenium, the key parameters for calibration are selenium concentrations in riverine inputs, which showed a range from 0.35 – 0.75 μg/g (Doblin et al. 2006). The derived selenium concentrations in PSP are slightly higher than values used in Meseck (2002) at 0.05-0.10 μg/g for each species.

The total riverine particulate selenium input for the year 1999 based on high flow particulate selenium concentration is 465 kg/yr. Calibrated selenium content on particulates by species at the head of the estuary generally shows relatively low standard deviation (Table 3-3). The total particulate selenium at Rio Vista is 0.46 μg/g (sum of organic, inorganic, and elemental selenium). Higher selenium content on particulates may be expected during low flow (e.g., 0.75 μg/g in Nov. 1999). Therefore the model was also run using a higher riverine particulate selenium concentration of 0.75 μg/g for low flow period (river flow $< 1.5 \times 10^{10}$ l/d).

3.2. CALIBRATION RESULTS

Calibrated salinity profiles for months between January 1999 - November 1999 compare well to the monthly cruise data obtained from the USGS ($r > 0.95$; GOF = 85.0 - 99.8 %; Figure 3-2). The model is able to simulate salinity profiles along the longitude of the estuary under different flow conditions, for both high and low flow time periods (e.g. April 1999 and November 1999). Lower salinity was simulated during high flow and salinity increases as flow decreases. The high correlation between the observed and predicted salinity for all data points in 1999 indicates the model is able to simulate the salinity relatively well (Figure 3-3, $R^2 = 0.971$) without systematic error. The residuals plots indicate larger deviation (observed – predicted salinity) occur near the Central Bay (Figure 3-4). The deviation is also larger for the months of April and June (Figure 3-5). These two months correspond to the falling limb of the hydrograph when flow is changing rapidly. It may be due to the rapid change of flow that the value of the dispersion coefficient also changes.

Calibration for TSM shows less agreement with the observed data than salinity, especially peak concentrations. The model is able to capture the locations of ETM for several months, although it under-predicted the peaks of ETM (Figure 3-6). Simulated TSM for low flow periods compared moderately well with the observed values ($r = 0.28 – 0.92$; GOF = 55.1 – 99.6 %). The model under-predicted a few TSM peaks because fitting using the same set of parameters for both high and low flow is difficult. If ETM is captured well during high flow, the TSM may be over-predicted during low flow. Correlation between predicted and observed TSM for all data points in 1999 is reasonable given the complexity of the underlying processes (Figure 3-7, $R^2 = 0.536$). The data points evenly scatter around the 1:1 line (Figure 3-7), except when observed concentrations are greater than about 50 mg/l.

Fitting of phytoplankton data in the NSFB is difficult due to multiple factors affecting the phytoplankton dynamics. Also, using one general function for growth and grazing may not capture the local variability over extended periods of time. As with TSM, the model was better able to capture average concentrations than the spatial and temporal locations of peak values. The model under-predicted the observed increases in phytoplankton concentrations in the Central Bay for several months (September and October 1999; Figure 3-8). Phytoplankton concentrations at the head of the estuary seem to have a large impact on the simulated phytoplankton concentrations in the bay. Generally, the fit for phytoplankton is reasonable for most of the months ($r = 0.04 – 0.80$; GOF= 42.5 – 94.3%). For several months (e.g. June 1999), high chlorophyll a concentrations were observed in the upper estuary. These high concentrations are likely due to lower zooplankton abundance in the upper estuary during spring months. The data points of predicted and observed chlorophyll a concentrations for 1999 scatter around the 1:1 line, with some under-prediction at high numbers and some over-prediction ($R^2 = 0.36$). The under-prediction is most notable near the Central Bay. The high chlorophyll a concentration near Central Bay could be a result of advection from South Bay or changes in phytoplankton species in the Central Bay.

Simulated dissolved selenium concentrations during high flow for April 1999 indicated relatively conservative behavior of mixing along the estuary and compared relatively well with the observed data (Figure 3-10). The fit for selenate and selenite is reasonable as indicated by relatively high goodness of fit (GOF = 82.1% and 70.6%). Observed organic selenide shows large variations along the estuary. Organic selenide was measured as the

difference between total dissolved selenium and other species of dissolved selenium, therefore the data inherently represent larger uncertainties. Because total selenium was measured separately, these concentrations were reported more accurately.

Simulated dissolved selenium concentrations during low flow for November 1999 show good agreement with the observed data (Figure 3-10). The model is able to capture the elevated selenium concentrations during low flow. A mid-estuarine peak is evident given the local sources from tributaries and refineries, despite refinery load reductions in mid-1998. The model does well in capturing mid-estuarine peak concentrations in selenite, selenate, and organic selenide (Figure 3-11).

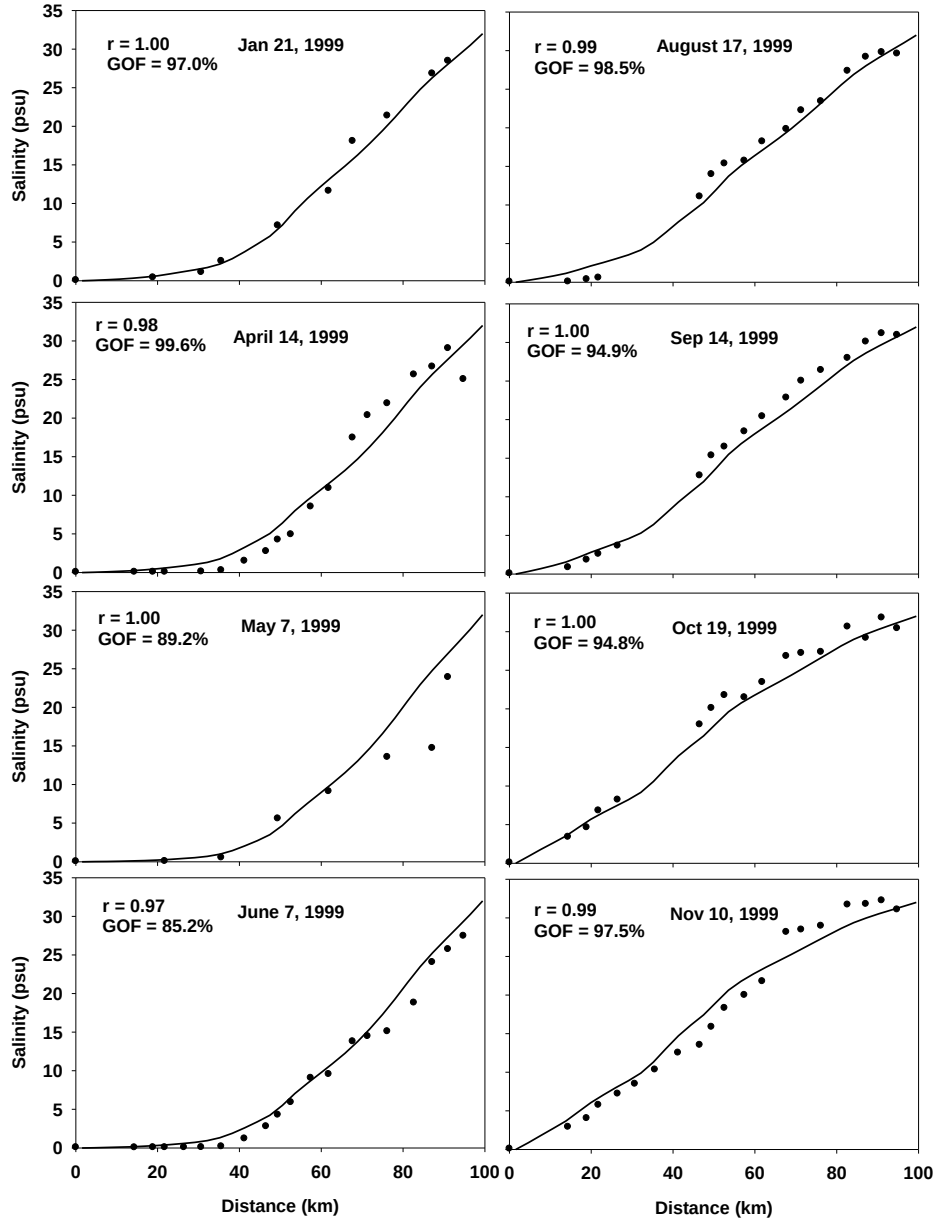


Figure 3-2 **Simulated monthly salinity profiles compared to the observed data from the USGS**

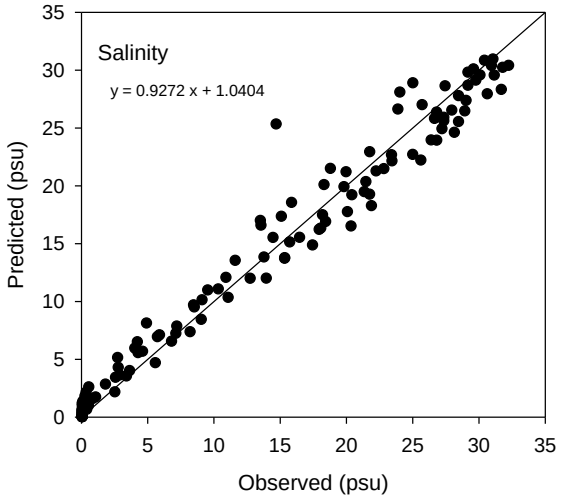


Figure 3-3 Comparison of predicted and observed salinity for different months for the calibration period of 1999.

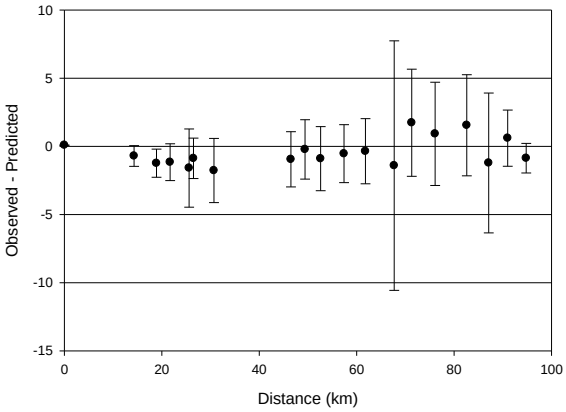


Figure 3-4 Deviation of observed and predicted salinity for 1999 across the estuary longitude profile

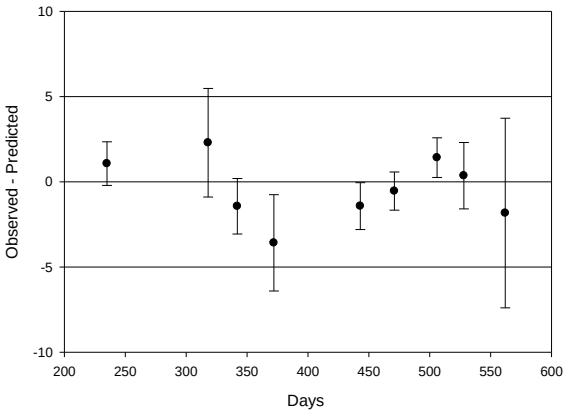


Figure 3-5 Deviation of observed and predicted salinity for sampling stations as a function of days from June 1st, 1998.

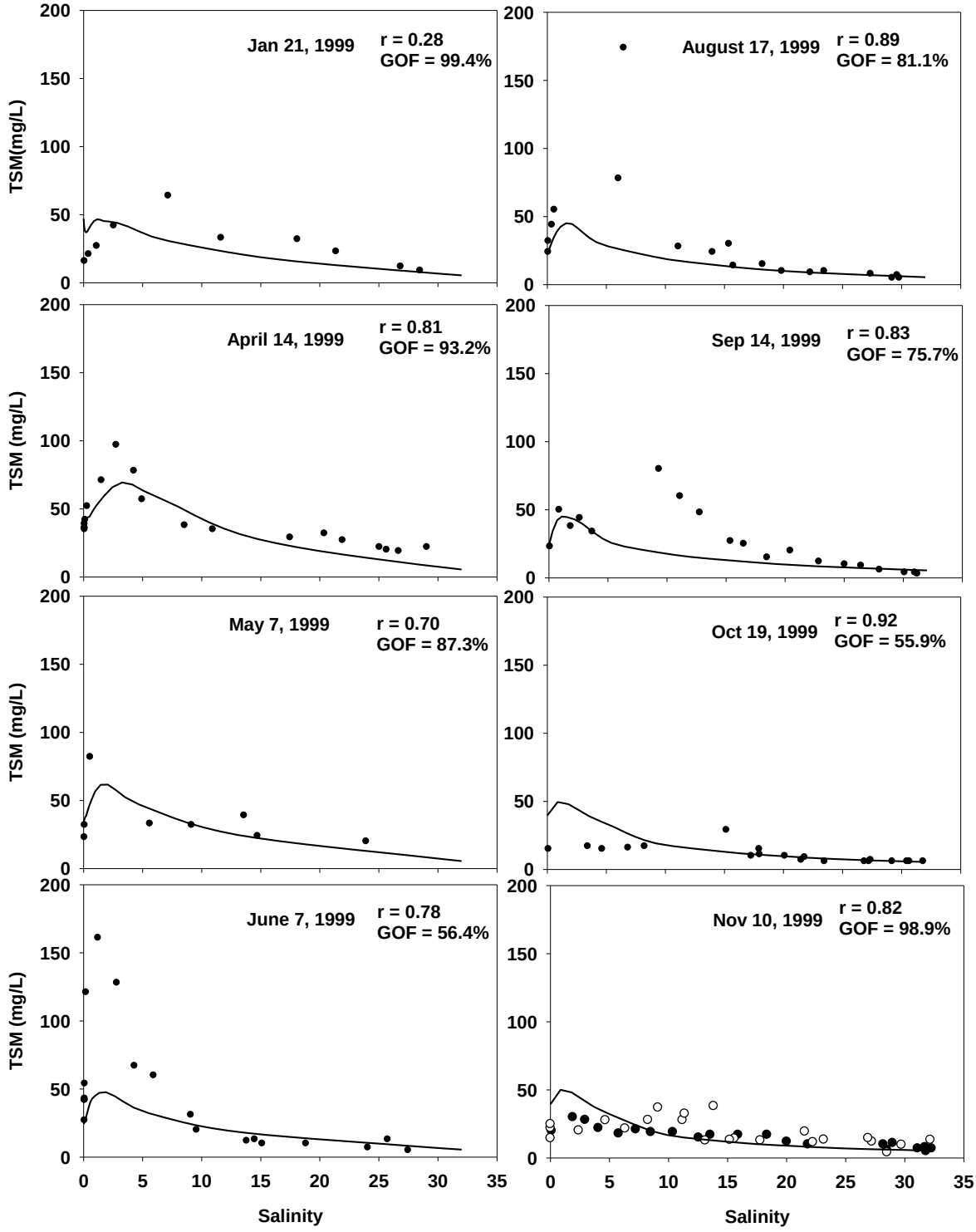


Figure 3-6 **Simulated TSM concentration profiles along the salinity compared to the observed data from the USGS. Data collected by Cutter and Cutter (2004) are shown with open circles.**

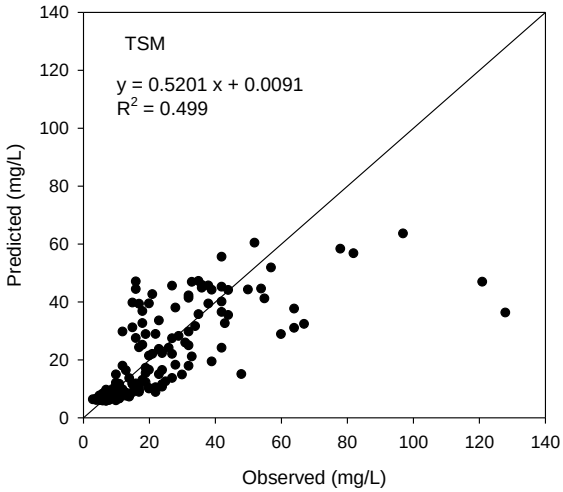


Figure 3-7 Comparison of observed and predicted TSM concentrations for different months in 1999.

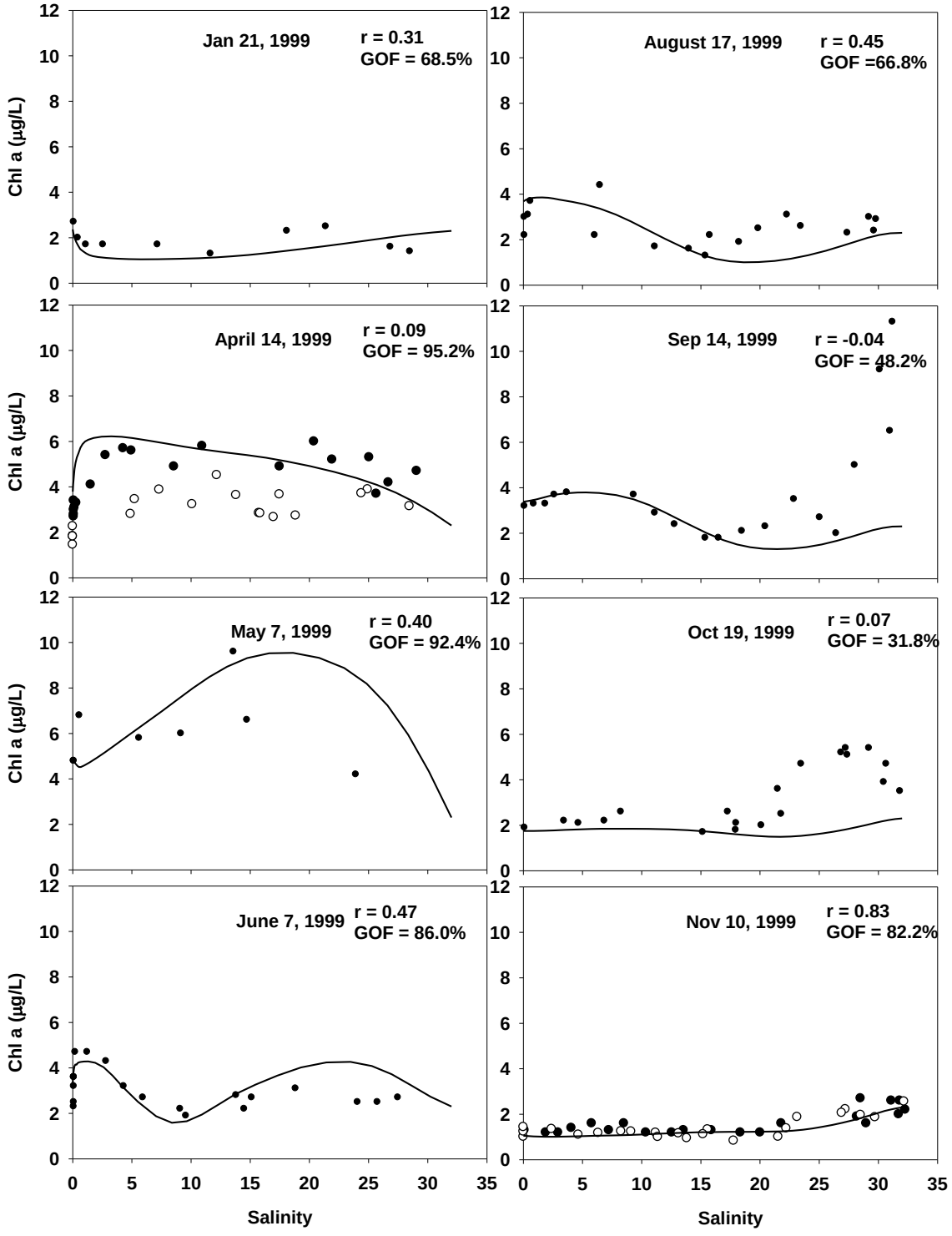


Figure 3-8 **Simulated phytoplankton profiles compared to the observed data from the USGS. Chlorophyll a concentrations sampled by Cutter and Cutter (2004) are shown with open circles.**

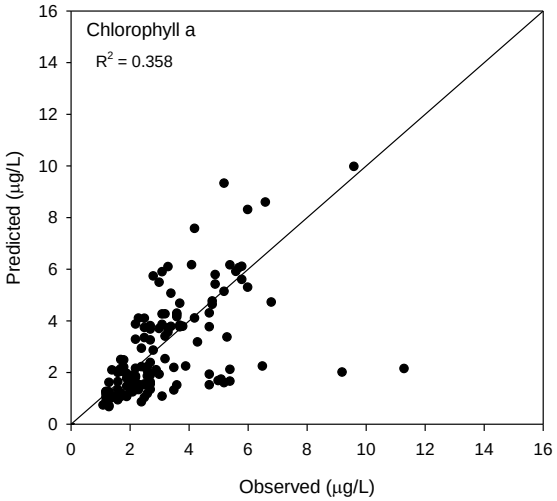


Figure 3-9 Comparison of observed and predicted chlorophyll a concentrations for different months in 1999.

Table 3-4
Evaluation of Goodness of fit for Model Calibration of Selenium for April and November 1999

		Selenate	Selenite	Org. Se	Particulate Selenite +Selenate	Particulate Elemental	Particulate Organic
April 13, 1999	r	0.400	0.067	-0.112	0.592	0.206	0.181
	GOF	78.4%	97.6%	46.3%	68.3%	83.2%	83.7%
November 11, 1999	r	0.539	0.314	0.568	0.487	0.208	0.087
	GOF	94.6%	97.5%	61.2%	90.2%	38.2%	94.7%

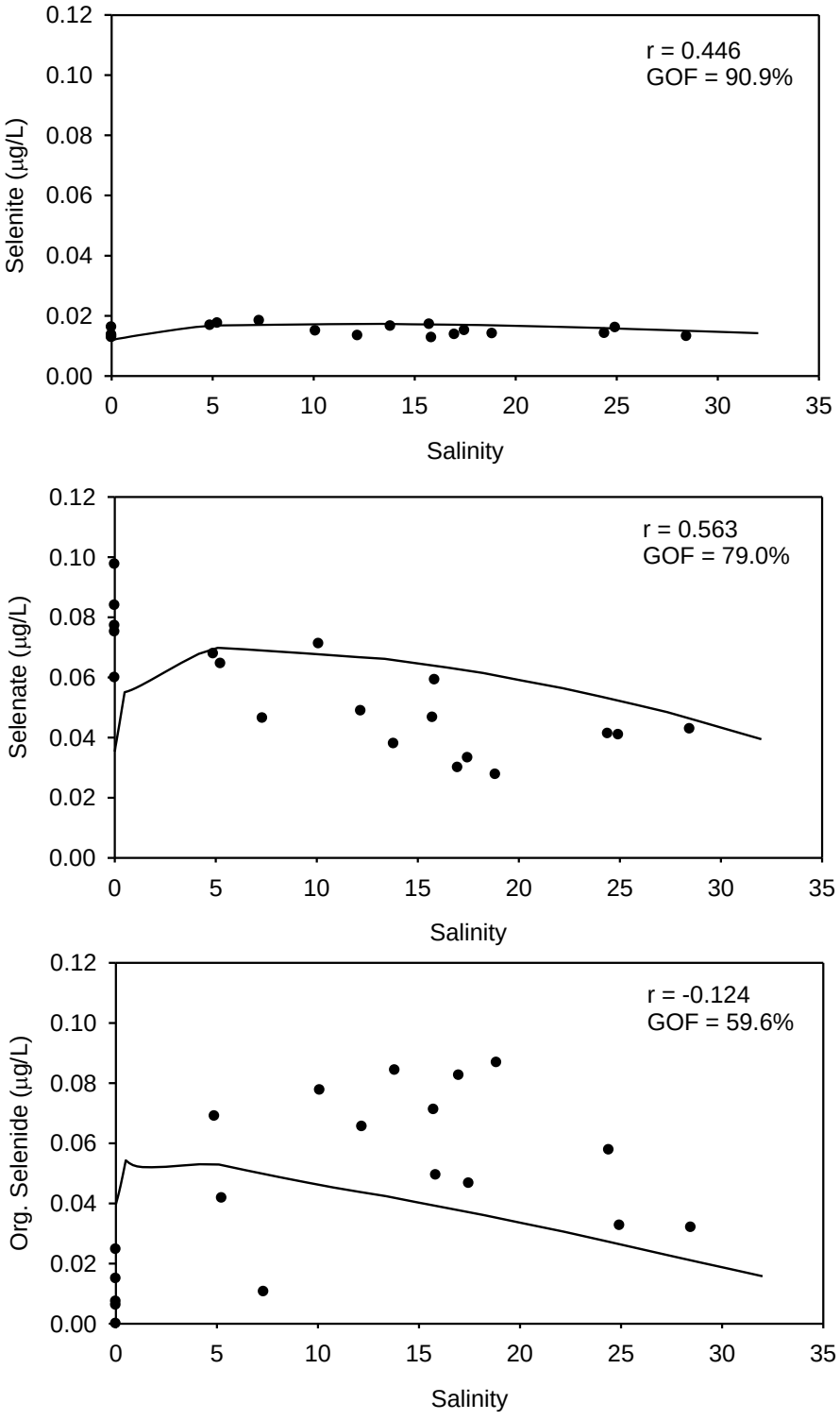


Figure 3-10 **Model simulated dissolved selenium concentrations in different species compared to the observed data for April 1999.**

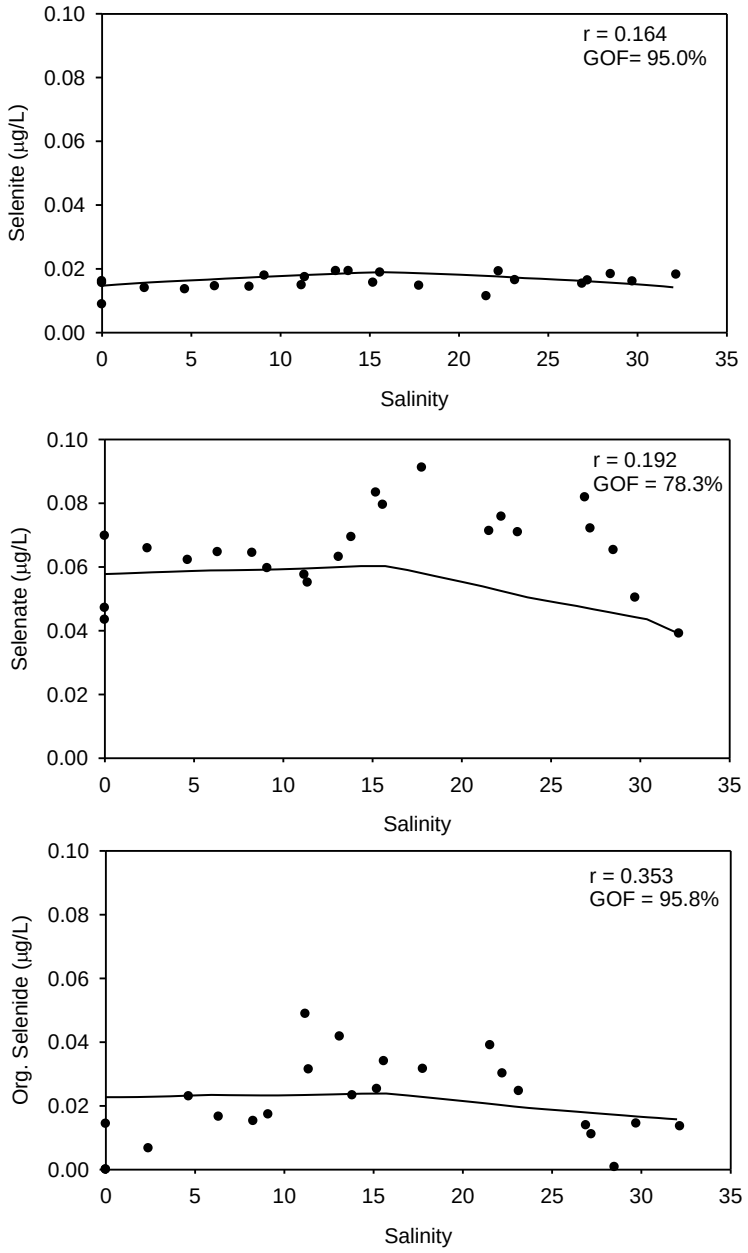


Figure 3-11 Model simulated dissolved selenium concentrations in different species compared to the observed data for November 1999.

Simulated particulate selenium concentrations (adsorbed selenite and selenate, elemental, and particulate organic selenide) show relatively conservative mixing behavior, decreasing with salinity and agree well with the observed data (Figure 3-12). Simulated particulate selenium concentrations for November 1999 along the salinity gradient generally agree with the observed data (Figure 3-13). Correlations between predicted and observed selenium concentrations are generally weak. However, predicted mean concentrations of different species of selenium (over different stations) compared well with the observed mean values (Table 3-5).

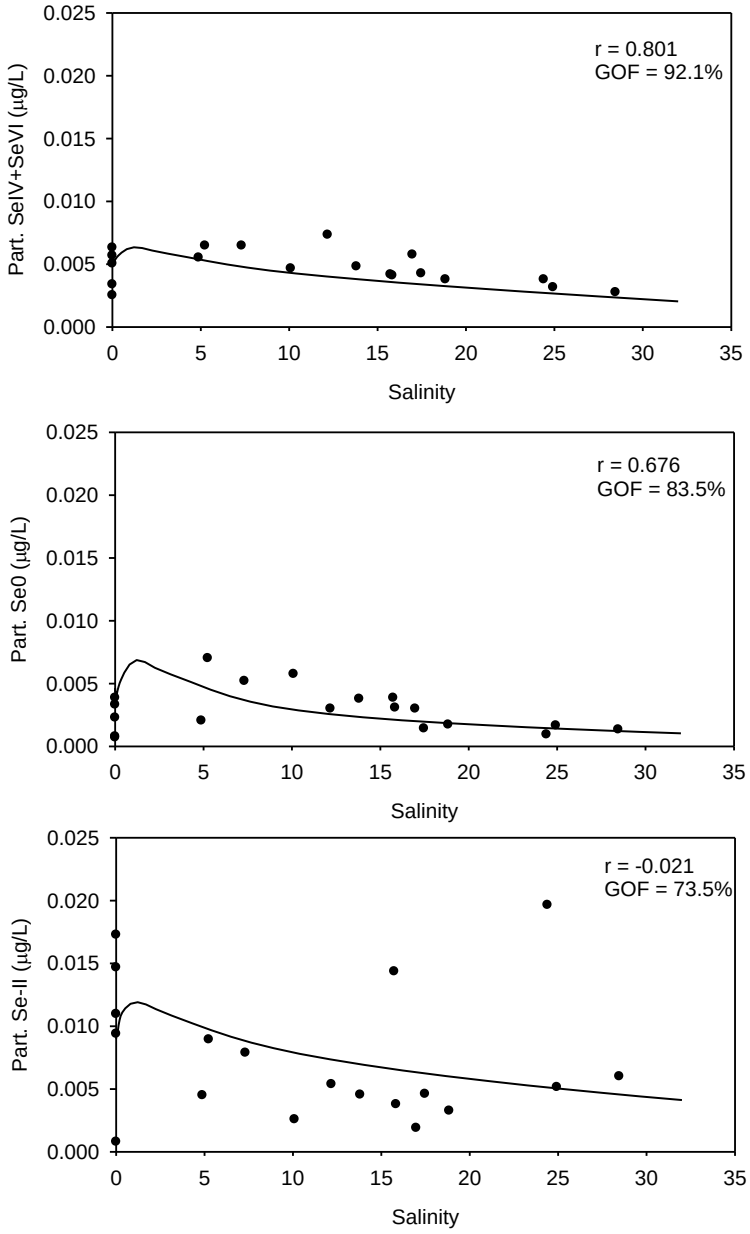


Figure 3-12 Simulated particulate selenium concentrations in different species compared to the observed data for April 1999.

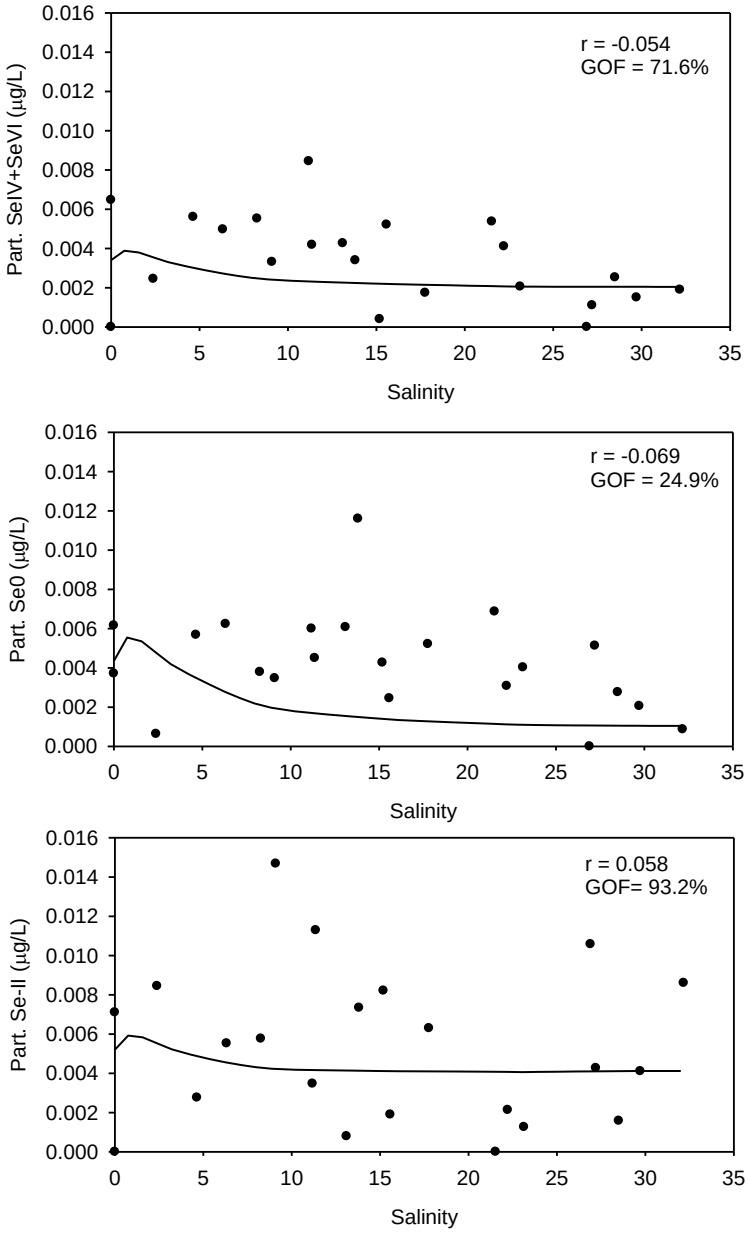


Figure 3-13 Simulated particulate selenium concentrations in different species compared to the observed data for November 1999.

Table 3-5
Comparison of predicted and observed mean salinity, TSM, chlorophyll a, selenite, selenate, organic selenide, particulate organic selenide, particulate adsorbed selenite + selenate, and particulate elemental selenium and percent error for calibration period of 1999

Parameter	Units	Predicted	Observed	Percent Error (%)
Salinity	Psu	13.153	14.272	-7.84
TSM	mg/L	0.023	0.024	-4.17
Chlorophyll a	µg/L	2.67	3.15	-15.24
SeIV	µg/L	0.016	0.015	6.67
SeVI	µg/L	0.053	0.06	-11.67
OrgSe	µg/L	0.029	0.033	-12.12
POrgSe	µg/L	0.008	0.008	0.00
Pseivvi	µg/L	0.004	0.003	33.33
PSe0	µg/L	0.003	0.003	0.00

3.3. MODEL EVALUATION

Because the model calibration was performed for only one year (1999), model evaluation against other time periods with different flow conditions is necessary. Model evaluation was performed using data for 1986 and for years after 1999. Calibration using both 1999 and 2001 data does not show significant changes in calibrated parameters for salinity and phytoplankton. However after 1999, detailed selenium concentration data by species are not available. The only data available are the total selenium concentration data collected by Regional Monitoring Program (RMP; http://www.sfei.org/rmp/ rmp_data_access.html).

3.3.1 Evaluation of Salinity, TSM, Phytoplankton and Selenium for Individual Sampling Dates in 2001 and 2005

The calibrated model was evaluated against estuarine profile data for salinity, TSM, and phytoplankton for water year 2001 and 2005 collected by USGS, and long-term total selenium data collected by RMP for water year 2001 through water year 2005. Of these limited additional years of sampling, our goal was to select wet and dry years for comparison to the 1999 calibration year. Water year 2001 was selected because it was a dry year, with flows much lower than 1999 and water year 2005 was selected because it was a relatively wet year based on the classification from DWR (http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST). More specifically, 2001 was classified as a dry year for both the Sacramento and San Joaquin River basins, and 2005 was classified as an above normal year for the Sacramento basin and a wet year for the San Joaquin basin.[3] No critically dry years occurred during the 2001-2005 period. The evaluation was for both simulations along the estuary longitude for various sampling time periods and simulations at fixed locations over

[3] In summary, the water year (October 1 to September 30) discharges for 1999, 2001, and 2005, in million acre-feet, were as follows:

	1999	2001	2005
Sacramento River Basin	21.19	9.81	18.55
San Joaquin River Basin	5.91	3.18	9.21

long-term time periods, for both physical and biological parameters and selenium concentrations.

Time periods of model calibration/evaluation are shown in Figure 3-14. The calibration dates for physical parameters have a flow range of 150-1,425 m^3/s, which contains the range of flows used for the evaluation period (Figure 3-14).

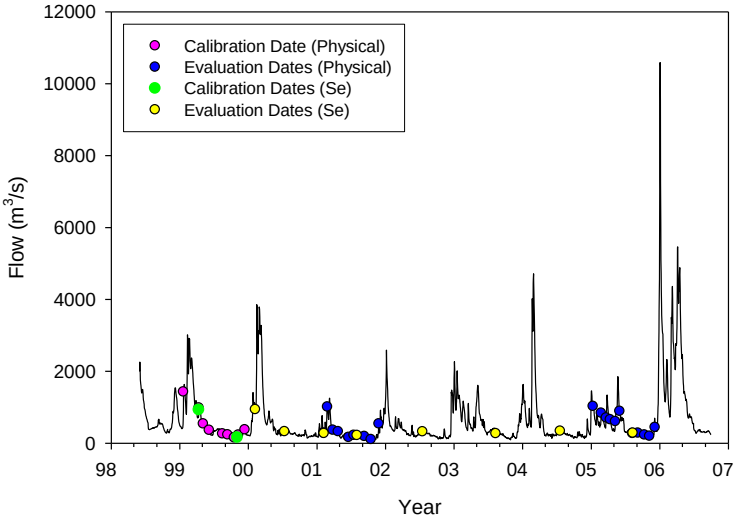


Figure 3-14 Dates for model calibration and evaluation for various parameters.

Evaluation of salinity for the low flow year 2001 suggested good agreement of simulated salinity versus observed values for different months across the year. The salinity was over-predicted or under-predicted for a few high flow months. However, overall values for goodness of fit for these months are between 71.5-97.9% (Figure 3-15). Evaluation of TSM against the observed values for the low flow year 2001 also suggested good agreement between the observed and simulated values (GOF = 36.4 – 99.4%) (Figure 3-16). The location of estuarine turbidity maximum (ETM) was simulated well for most months in 2001, particularly for June and July 2001. TSM was under-predicted occasionally, similar to the pattern in model performance for the calibration period. The under-prediction in ETM may result in higher predicted selenium content on particulates.

Evaluation of simulated chlorophyll a concentrations for 2001 against the observed values indicated that the mean values of chlorophyll a concentrations were predicted well in the estuary for most months (Figure 3-17; GOF = 53.7 – 95.7%). For about two months, chlorophyll a concentrations were under predicted near the Central Bay, similar to the pattern in the calibration. For the evaluation period, simulated correlation coefficient (r) is 0.92-1.00 for salinity in 2001, 0.68 – 0.97 for TSM in 2001, and 0.02-0.79 for chlorophyll a in 2001. Chlorophyll a concentrations in 2001 do not show a peak in the upper estuary as shown in the calibration period therefore the simulated concentrations compared well with the observed values for that region.

Evaluation of salinity for above normal flow year 2005 showed very good agreement with the observed data (Figure 3-18; GOF = 50.4 – 99.7%). The evaluation of TSM for 2005

shows good agreement for the first several months, particularly for January, March and June 2005 (Figure 3-19). For April and May 2005, the ETM was under-predicted (Figure 3-19; GOF = 48.2 – 97.7%). This is similar to the results in calibration where ETM was under-predicted in some occasions.

Currently salinity is simulated using a constant Kw overtime for the validation period of 2000-2006. Alternatively Kw can be simulated as a function of flow and salinity in the estuary, as in Harris and Gorley (1998). The results in salinity are very similar to current results reported, with slightly lower goodness of fit. Alternatively, salinity could also be simulated as a function flow, salinity and salinity gradient, as in Meseck (2002). The results are a better ETM in TSM simulation for high flow months (particularly for June 1999), however also predicts ETMs in TSM for months without observed ETM. The formulation also results in a relatively linear predicted salinity profile along the estuary.

Evaluation of chlorophyll a for 2005 indicated that the model was able to capture chlorophyll a concentrations both temporally and spatially for most of the months (Figure 3-20; GOF = 13.5 – 98.5%). Chlorophyll a concentrations were under-predicted during spring months. The phytoplankton is simulated as light dependent. Simulated photosynthetically active radiation (PAR) that affects phytoplankton growth is low during spring months; however, significant phytoplankton blooms still occurred during spring as shown in the observed data. The elevated phytoplankton concentrations could be due to elevated nutrient concentrations, advection from South Bay, less grazing in Central Bay, different species of phytoplankton, higher maximum photosynthesis rates, less light extinction in the Central Bay or other processes that contribute to phytoplankton bloom that are not captured by the model. Currently the model under-predicted some of these blooms during spring. Advection from South Bay was currently simulated as freshwater inflow of South Bay multiplied by a chlorophyll a concentration of 6 μg/L. Phytoplankton concentrations as shown in Section 4 affect selenium concentrations in particulates and therefore in bivalves. The under-prediction could potentially result in under-prediction of selenium content on particulates. For 2005, peaks in chlorophyll a concentrations in the upper estuary were not observed, as opposed to patterns shown in the calibration period.

For the evaluation period, the correlation coefficient r is 0.92 – 1.00 for salinity in 2005, 0.09-0.94 for TSM, and -0.64 – 0.85 for chlorophyll a. Correlation between predicted and observed salinity, TSM and chlorophyll a concentrations for 2001 and 2005 is shown in Figure 3-21. The correlation between predicted and observed values was reasonable. For the evaluation period, some adjustments in zooplankton grazing rates were still needed to better simulate variations in phytoplankton concentrations.

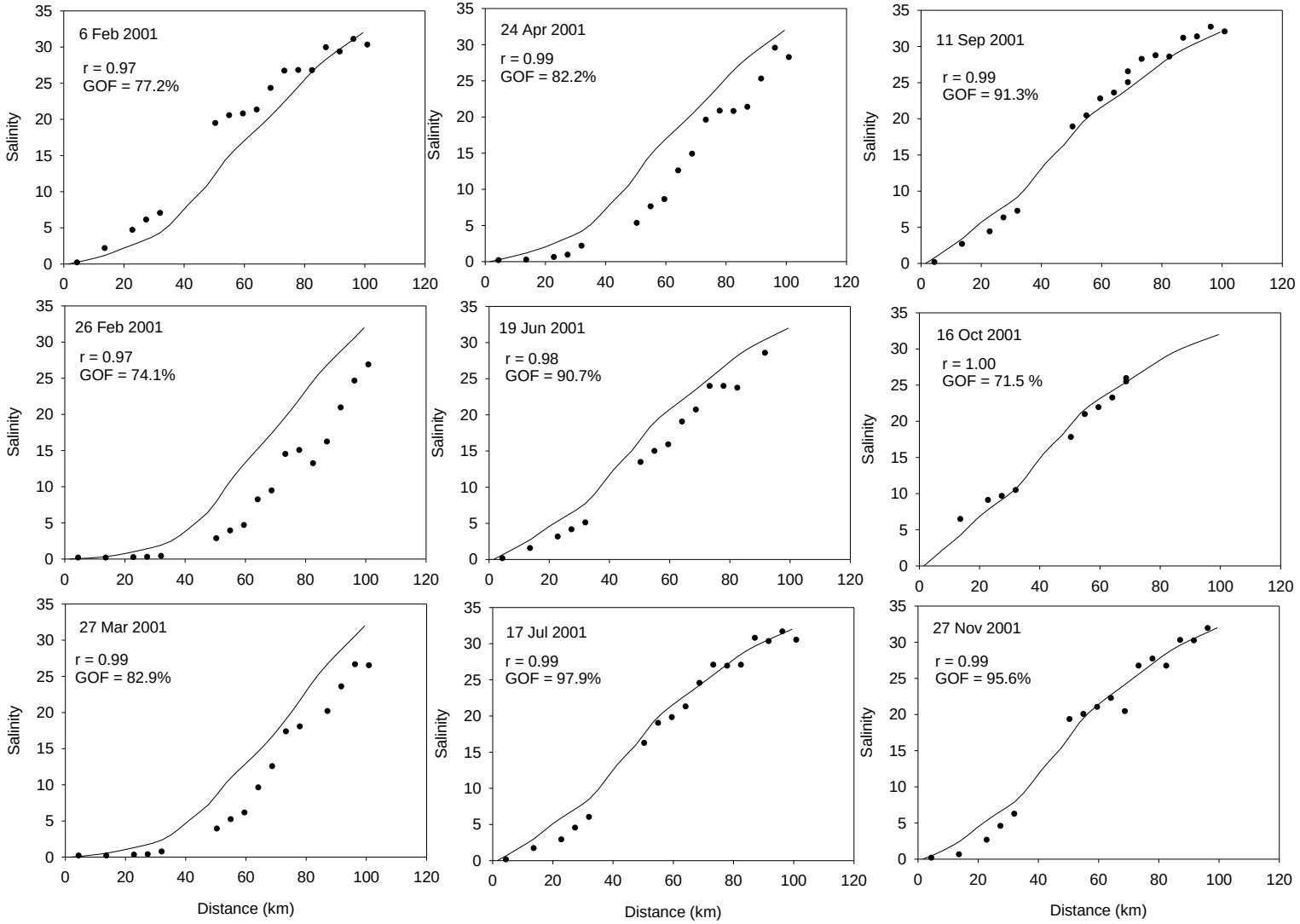


Figure 3-15 Evaluation of simulated monthly salinity profiles for a low flow year 2001 (Data source: USGS)

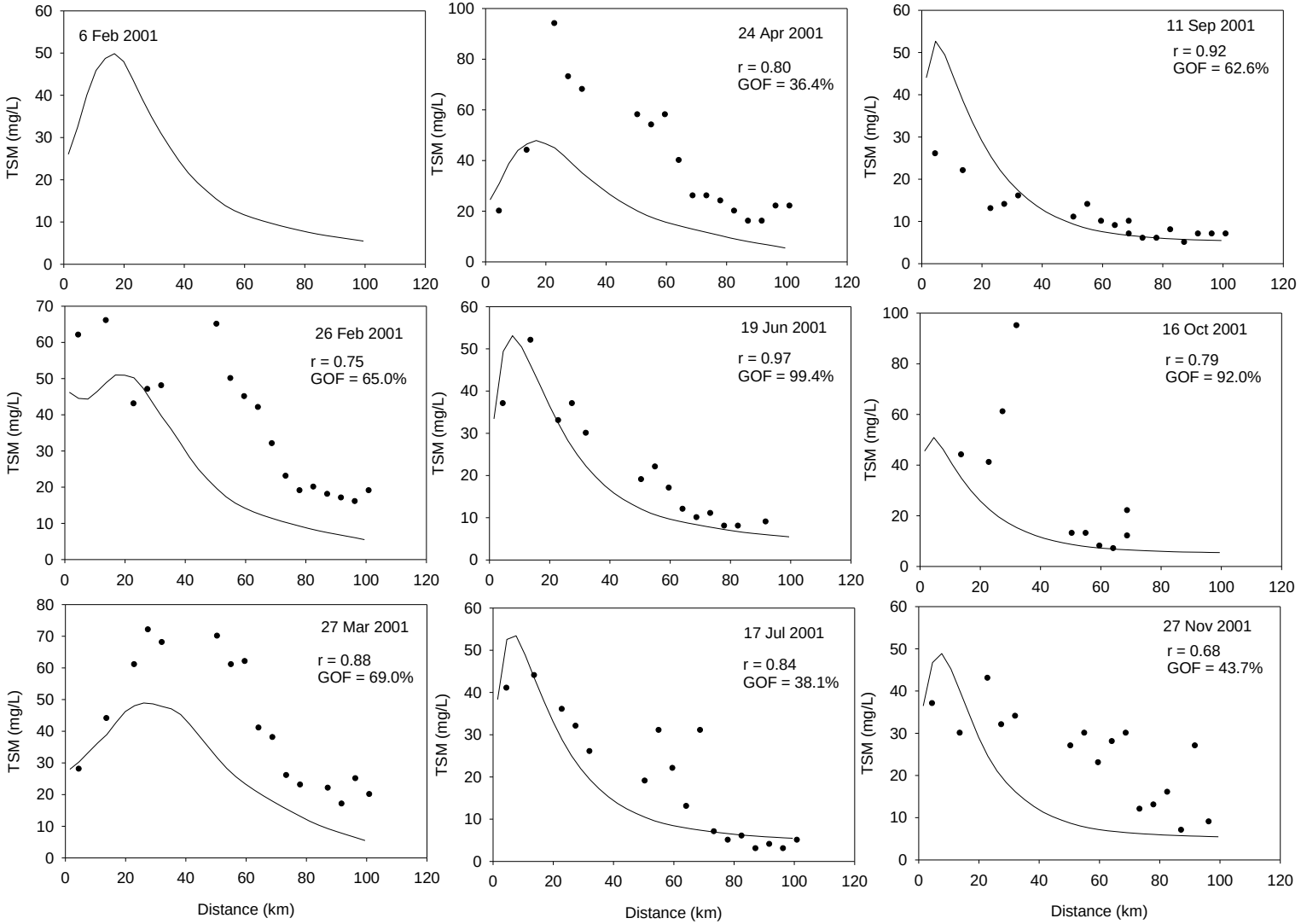


Figure 3-16 Evaluation of simulated monthly TSM profiles for a low flow year 2001 (Data source: USGS).

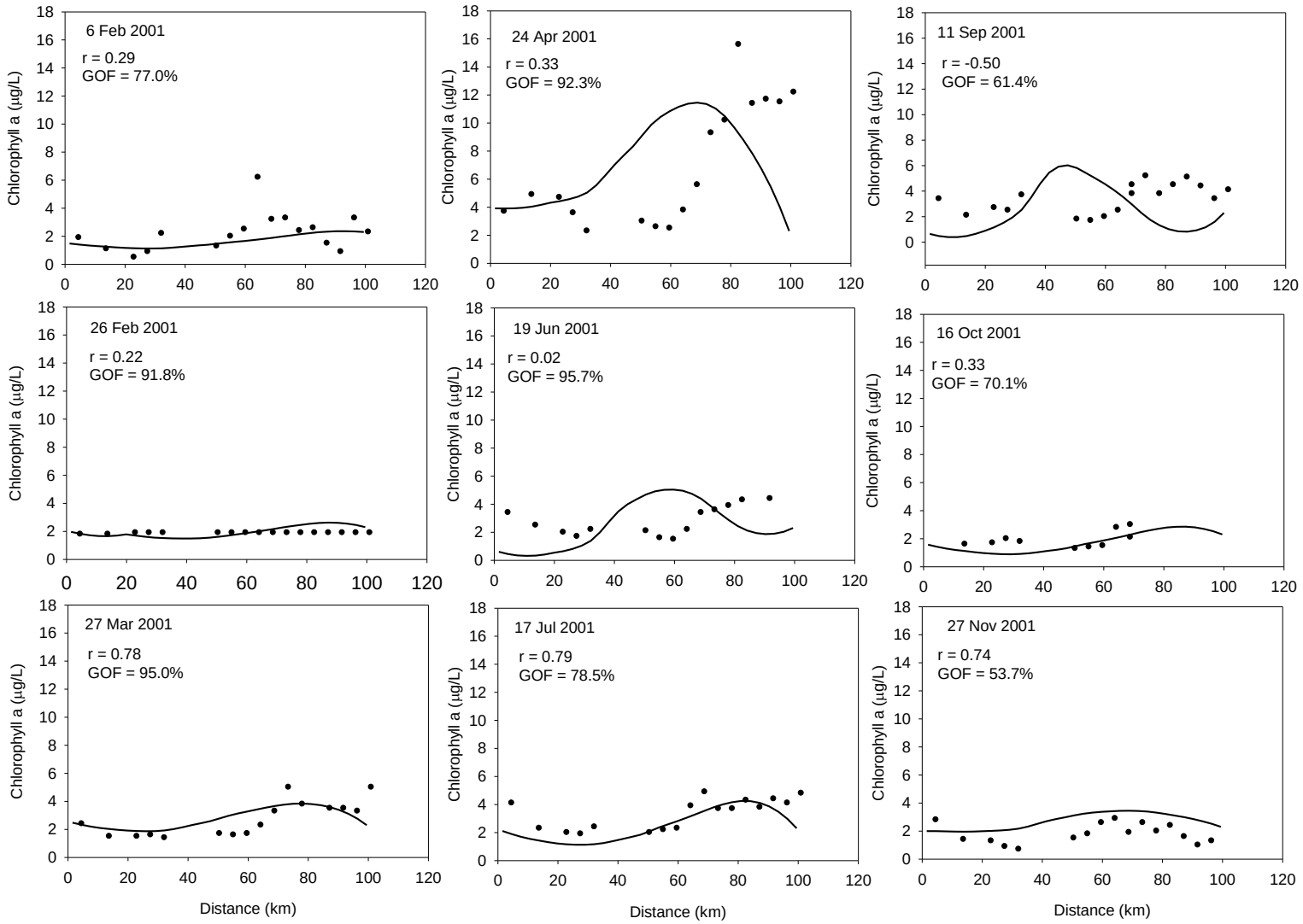


Figure 3-17 Evaluation of simulated monthly chlorophyll a concentrations for a low flow year 2001 (Data source: USGS).

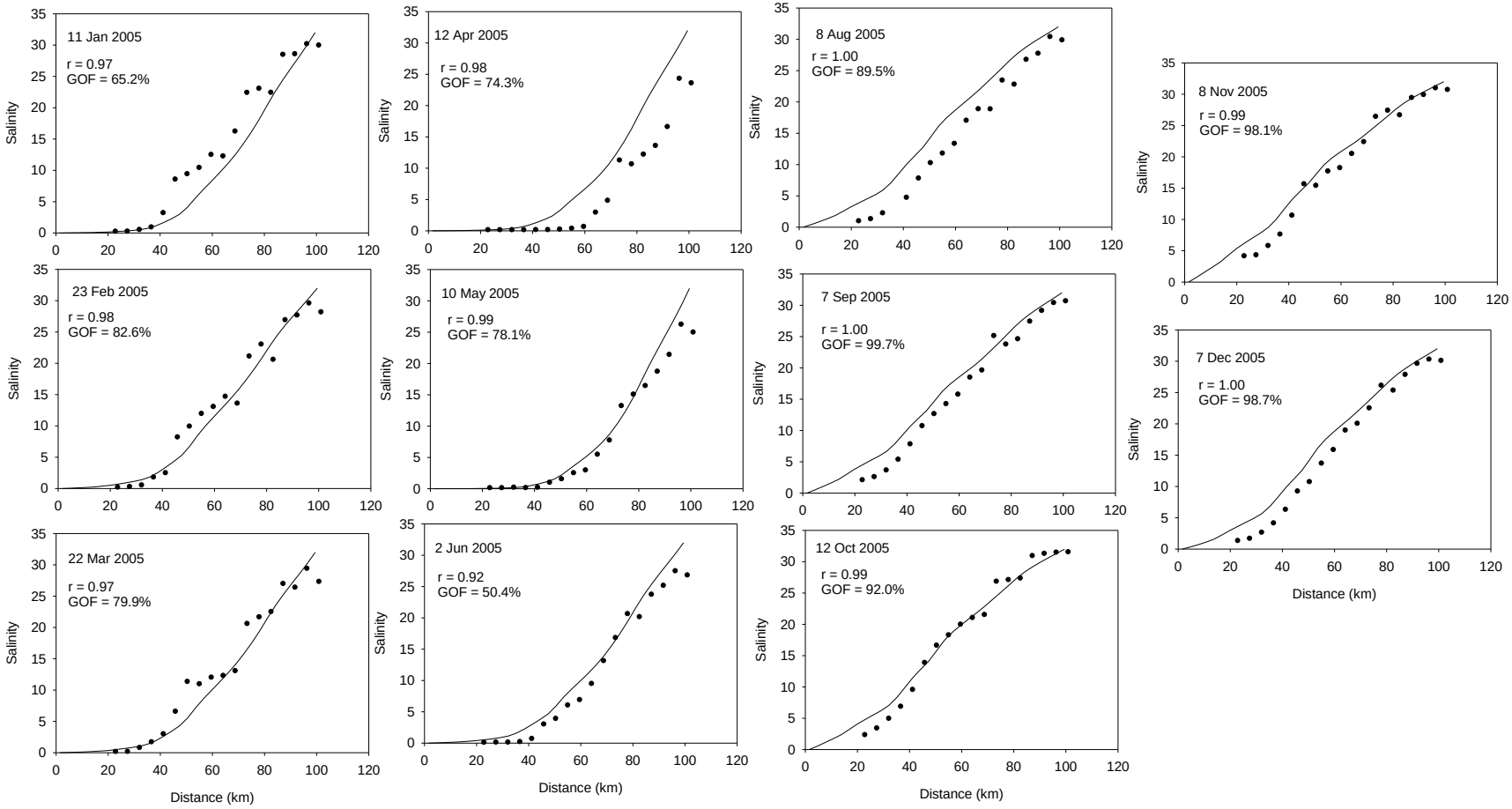


Figure 3-18 Evaluation of simulated monthly salinity profiles for a high flow year 2005 (Data source: USGS).

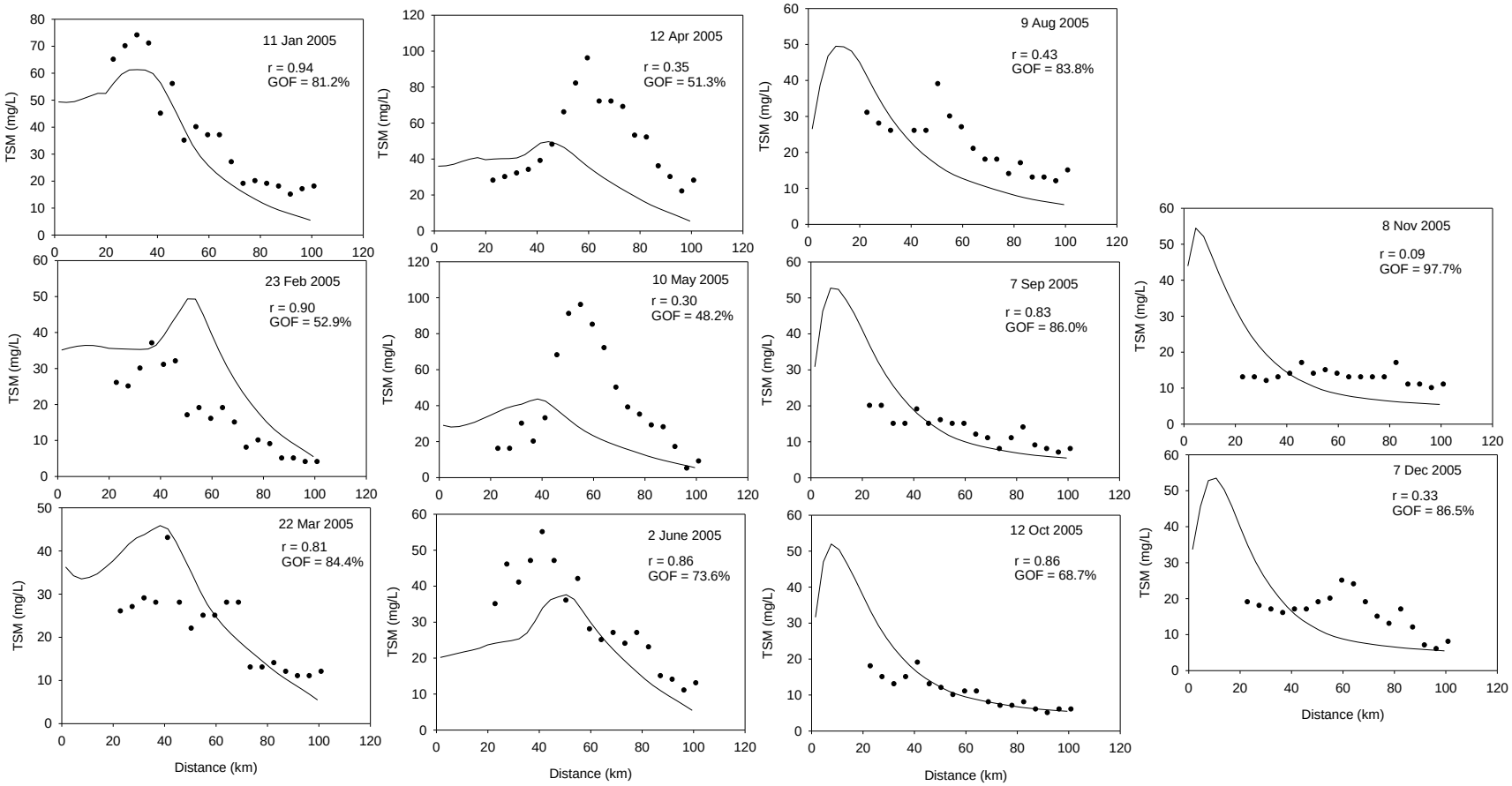


Figure 3-19 Evaluation of simulated monthly TSM profiles for a high flow year 2005 (Data source: USGS).

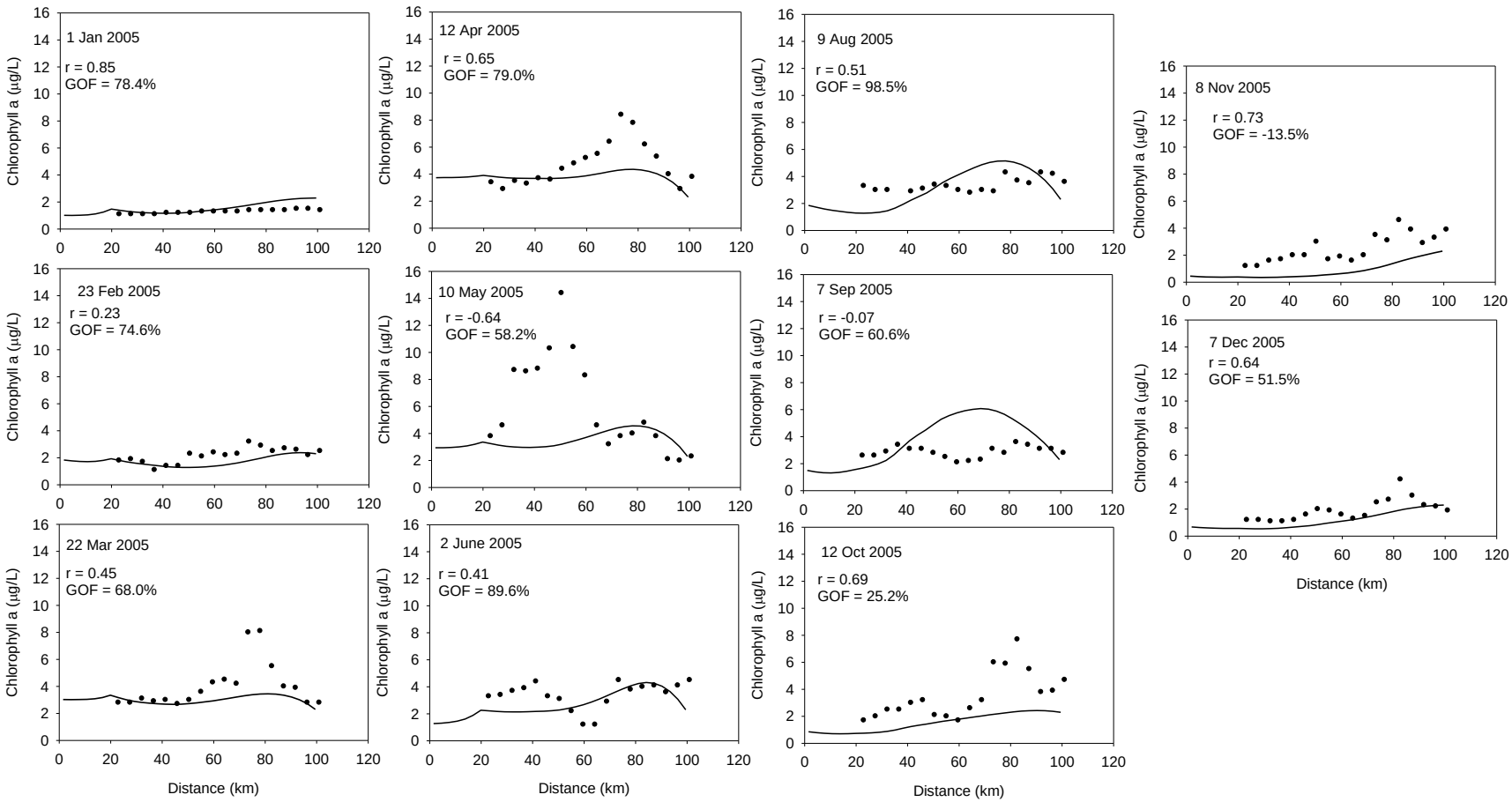


Figure 3-20 Evaluation of simulated monthly chlorophyll a concentration profiles for a high flow year 2005 (Data source: USGS).

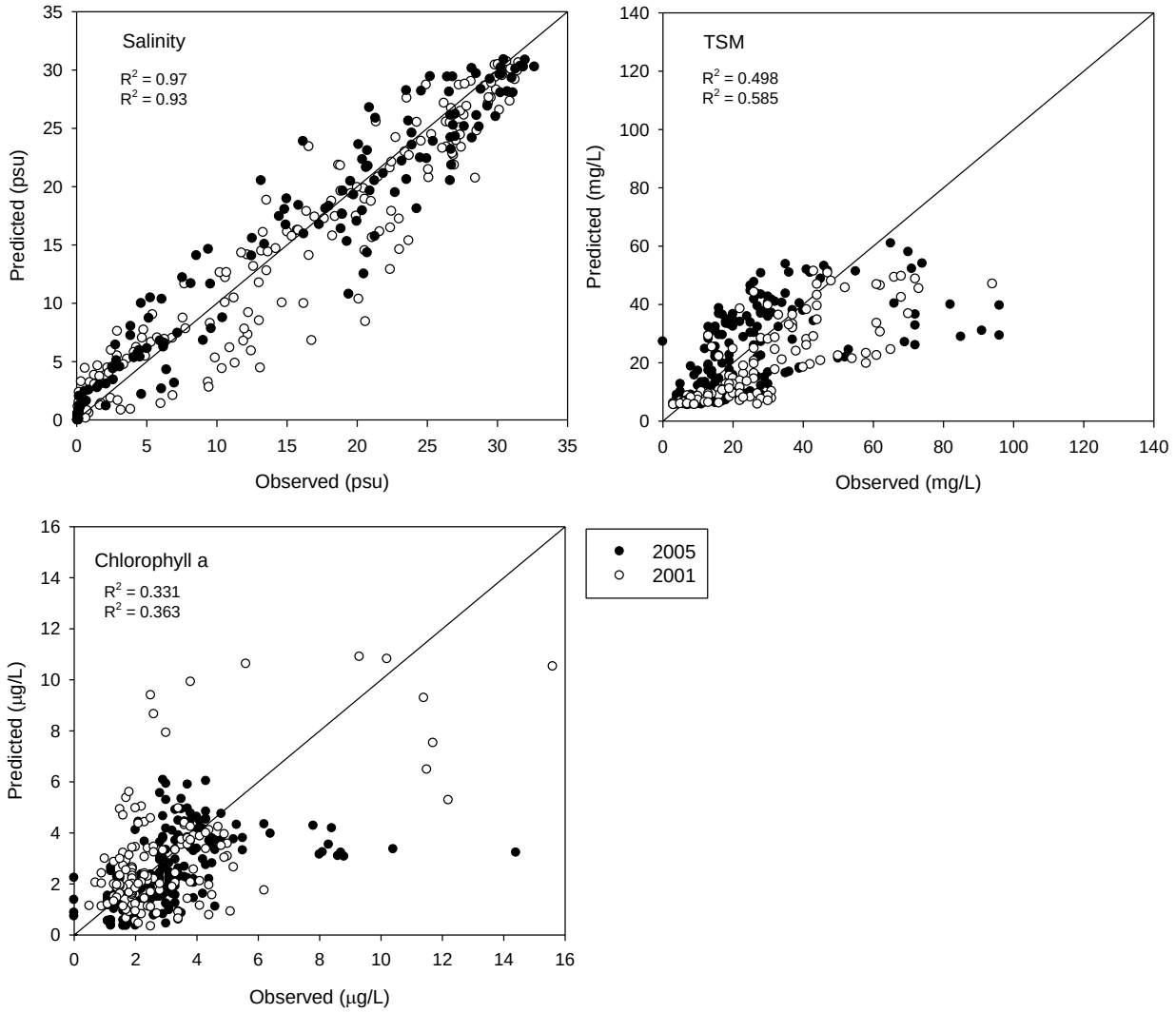


Figure 3-21 Model simulated salinity, TSM, and chlorophyll a concentrations for 2001 and 2005 compared to the observed values.

The model was run for multiple years from 2000 to 2005. Simulated model results for total selenium (particulate + dissolved) from February 2000 to August 2005 were also compared against the observed data from RMP across the estuary for multiple time periods. As noted earlier, this comparison was driven by the fact that the RMP data do not report speciated selenium concentrations. Comparison of simulated concentrations against the RMP data suggested that the model is able to simulate selenium concentrations well for a range of hydrological and load input conditions during 2000-2005, including both dry year and wet year flows, and dry season and wet season conditions (Figure 3-22). The simulation years are mostly for years after refinery clean-up, which occurred in mid-1998, and the mid-estuarine selenium peak is not very evident for most of the years simulated. Although the inter-annual variations in total selenium data are significant, simulated total selenium concentrations were generally in the range of the observed concentrations.

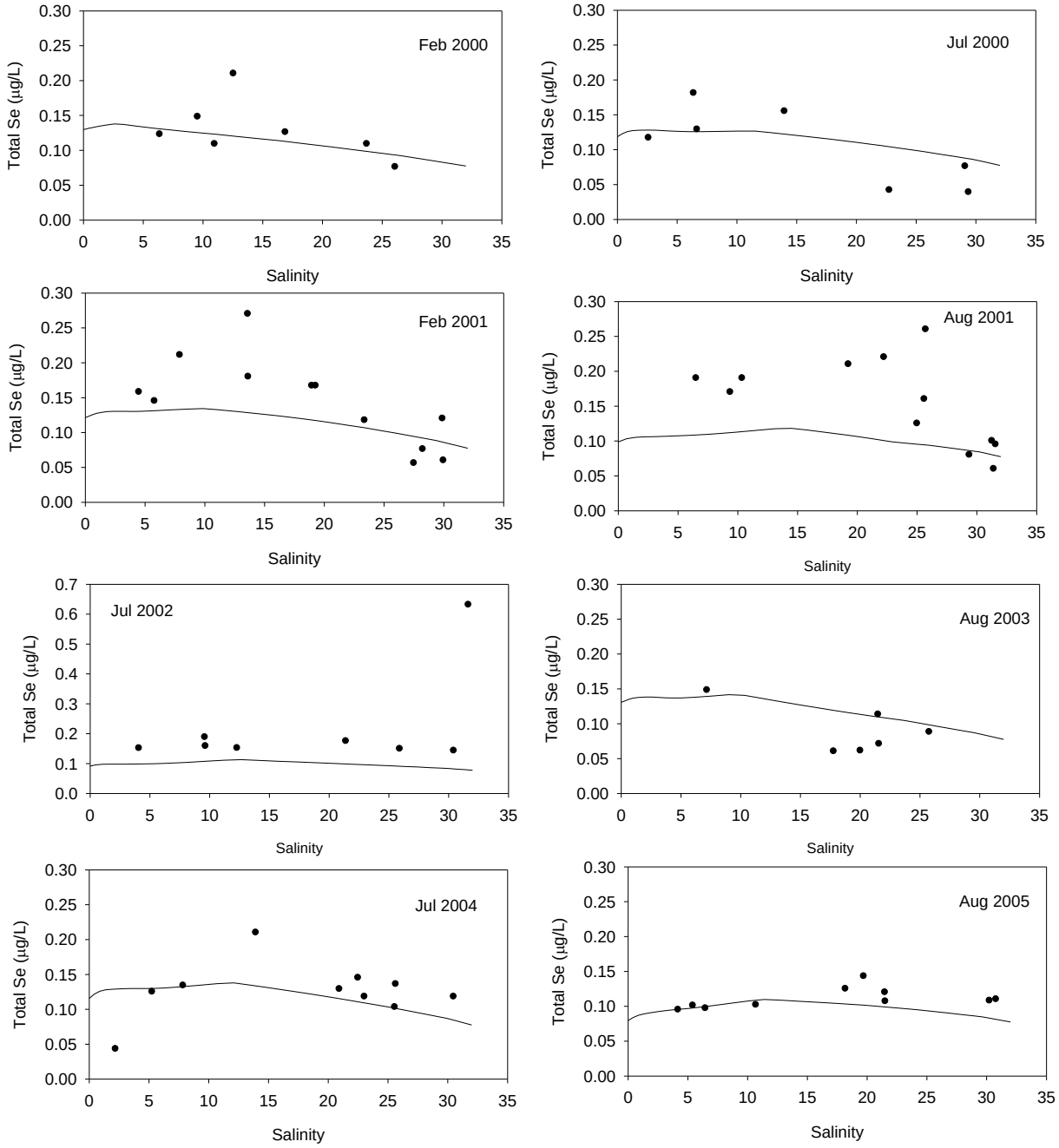


Figure 3-22 Model simulated total selenium concentrations (dissolved + particulate) compared to selenium data collected by RMP. Note that the RMP dataset does not report selenium species information.

3.3.2 Long-term Evaluation of TSM and Chlorophyll a Concentrations

Simulated TSM and chlorophyll a concentrations were also evaluated against data from the USGS long-term monitoring stations. The model-simulated chlorophyll a and TSM concentrations were evaluated against long-term data at four stations, station 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay) and 18 (Central Bay), respectively. The model is able to capture the seasonal patterns in chlorophyll a concentrations and TSM (Figure 3-23 and

Figure 3-24) relatively well. The model is able to capture the peaks and lows in both TSM and chlorophyll a concentrations.

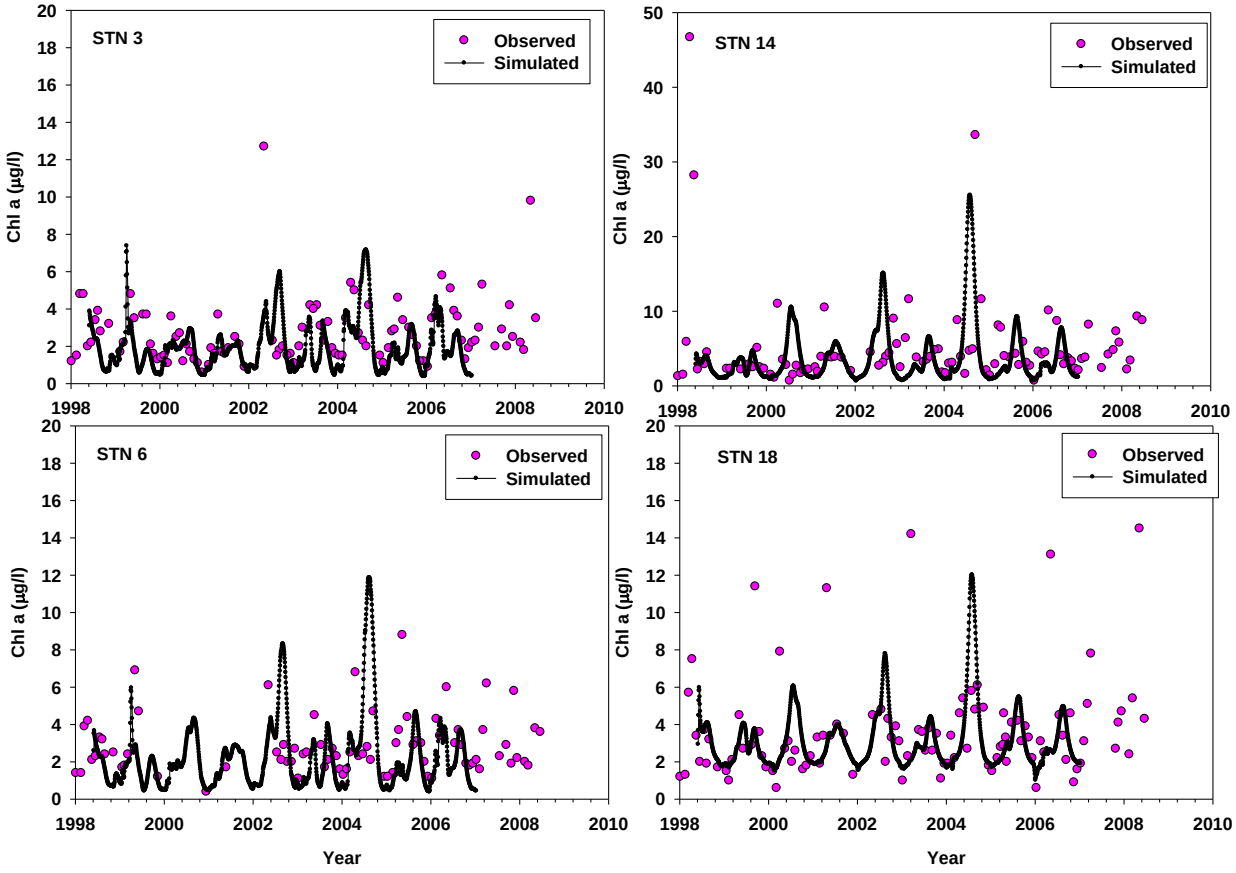


Figure 3-23 **Simulated time series of phytoplankton concentrations compared to observed data from USGS at stations 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay) and 18 (Central Bay). Locations of USGS stations are shown in Figure 1-2.**

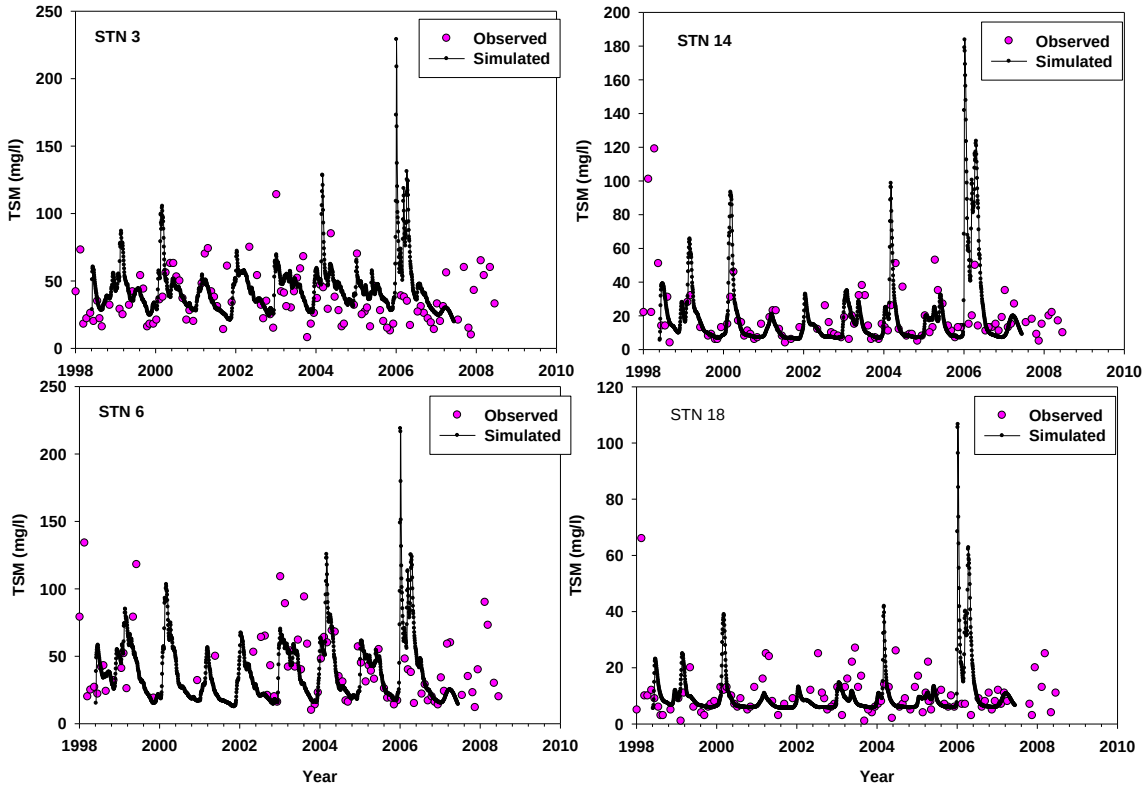


Figure 3-24 Simulated time series of TSM compared to observed data from USGS at stations 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay) and 18 (Central Bay).

3.3.3 Evaluation of Long-term Selenium Concentrations

Simulated dissolved selenium concentrations were also evaluated against the long-term record for several long-term RMP monitoring stations BF10 (Pacheco Creek) in Suisun Bay, BF 20 in Suisun Bay, BD30 (Pinole Point) in San Pablo Bay and BC10 in Central Bay (Figure 3-25). The results generally show good agreement between model simulated total selenium concentrations (particulate + dissolved) and the observed data for the simulation period of 1999-2006. Higher total selenium concentrations were observed for periods prior to the improved wastewater treatment from refineries. Selenium loads for this period (prior to 1999) should be greater than currently used in the model for 1999 onward. Some high total selenium concentrations in Suisun Bay are not captured well by the model. This may be due to variations in selenium inputs from rivers or tributaries or local-scale processes that are not represented well by the model. For San Pablo Bay, the observed variation in total selenium concentrations along the estuary is captured well by the model prediction. The Central Bay showed less variation both in observed and predicted values. The predicted variation is most likely due to variations in load inputs, particularly from tributaries and the Delta as shown in the previous section (Figure 2-15 and Figure 2-18).

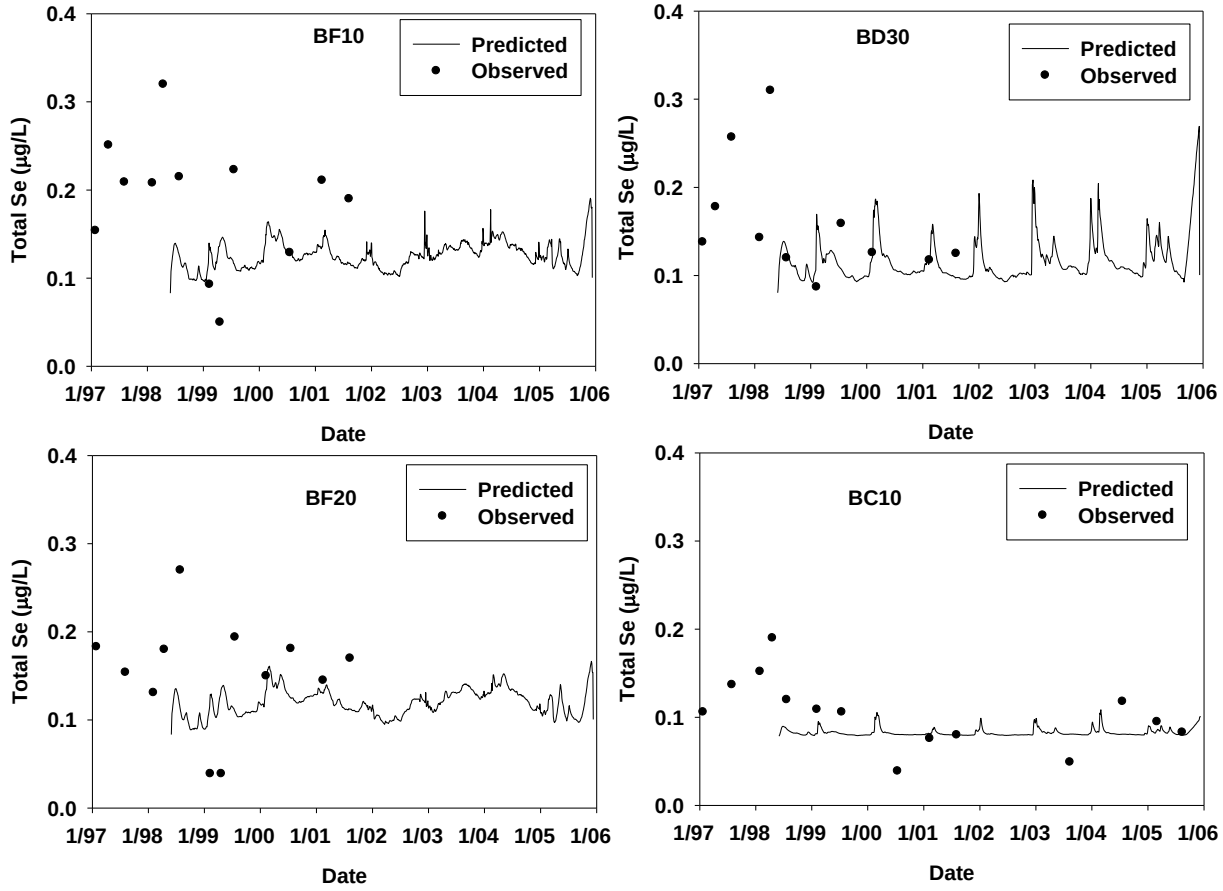


Figure 3-25 Model simulated total selenium concentrations at BF10 (Suisun Bay), BF20 (Suisun Bay), BD30 (San Pablo Bay) and at BC10 (Central Bay) compared to observed total selenium by RMP.

3.3.4 Model Predicted Particulate Selenium Concentrations

Simulated selenium concentrations on particulate matter (in µg/g) for November 11, 1999 were comparable to the observed data from Doblin et al. (2006; Figure 3-26). Particulate selenium is not directly measured by RMP. The predicted mean particulate selenium concentrations for NSFB for November 11, 1999 is 0.77 ± 0.35 µg/g, compared well to the observed value of 0.735 ± 0.25 µg/g (r = 0.45). The model-predicted upper-bound and lower-bound of the particulate selenium concentration is also shown. The upper-bound and lower-bound constituent values are derived by including an upper-bound and a lower-bound of several affecting parameters (derived in calibration), including selenium content on particulates at the head of estuary and San Joaquin load removal constants. The range of concentrations shown here suggests a relatively narrow range of uncertainties in parameter estimates.

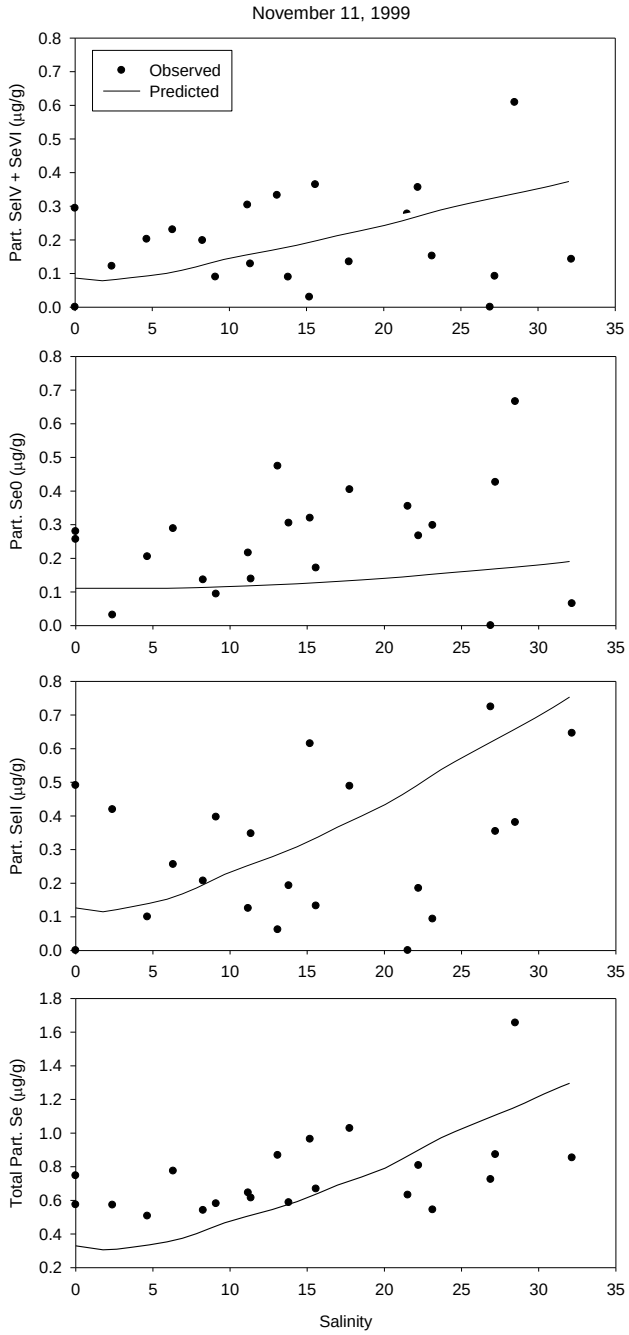


Figure 3-26 Simulated particulate selenium compared with the observed data from Doblin et al. (2006) for November 1999. The lowermost plot shows the range of particulate Se predictions using the high and low values of related calibration parameters.

Model simulated particulate selenium (in µg/g) and dissolved selenium (in µg/L) can be used to estimate the partition coefficients (K_d). Note that these are not true equilibrium partition coefficients in that the model uses a dynamic formulation for dissolved-particulate exchange; however, the instantaneous ratios of particulate and dissolved selenium, approximated as K_d, can be useful for comparing against the large amount of data from other systems where partition coefficients are reported. K_d values estimated in this work range

over an order of magnitude depending on the time and location of calculation. The variation is reflective of the changing sources and speciation of particulate selenium in the bay over time. Estimated K_d values range from 2.0×10^3 L/kg to 1.0×10^4 L/kg for a location in the San Pablo Bay (close to STN 14) for 1999 and from 2.73×10^3 and 1.72×10^4 L/kg as a function of distance for a low flow period (November 11, 1999; Figure 3-27). These ranges are in the range of K_d values summarized by Presser and Luoma (2006) for various ecosystems and the water column in Bay-Delta system (Table 3-6). However, the order-of-magnitude variability indicates the difficulty of using a single K_d value to accurately represent particulate concentrations over a range of conditions in the bay.

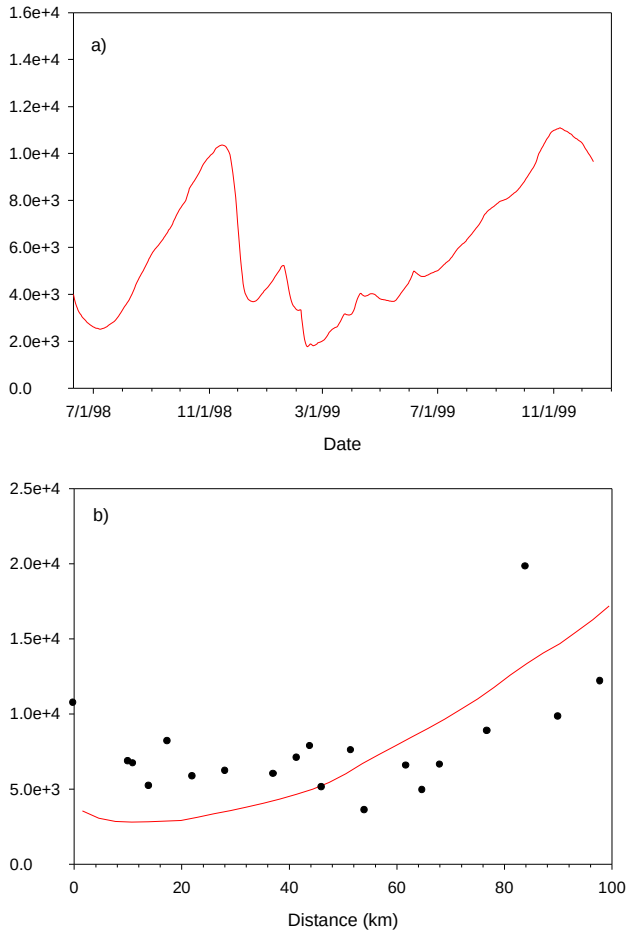


Figure 3-27 **Simulated partition coefficient (K_d, L/Kg) as a (a) function of time for year 1999 in San Pablo Bay and (b) as a function of distance for November 11, 1999. The Y axis ratio is instantaneous dissolved Se/particulate Se.**

Table 3-6
Partitioning Coefficients (Kd) Between Dissolved Selenium and Particulate Selenium in the Literature and Ssimulated by the Model (after Luoma and Presser, 2006)

Ecosystem or Organism	Selenium			Reference
	Dissolved (µg/L)	Particulate (µg/g)	Distribution coefficient, L/kg (K_d)	
Kesterson Reservoir Pond 2 Terminal Pond	 330 14	 55-165 13-24	 0.2 -0.5 × 10^3 0.9 -1.7 × 10^3	 Presser and Piper (1998) Presser and Barnes (1998)
Belews Lake	~11	~15	1.3 × 10^3	Lemly (1995)
Benton Lake Pool 1 channel Pool 2 Pool 5	 4 10.4 0.74	 10 3.5 0.35	 2.5 × 10^3 0.34 × 10^3 0.5 × 10^3	 Zhang and Moore (1996)
Constructed wetland	5.0-9.8	2.1-6.7	0.2 -1.2 × 10^3	Hansen et al. (1998)
San Luis Drain	330	84	0.25 × 10^3	Presser and Piper (1998)
Grassland Bypass Channel Project	62.5	30	0.5 × 10^3	Presser and Luoma (2006)
Delaware River (tidal freshwater)	0.17-0.35	0.6-1.5	4 × 10^3	Riedel and Sanders (1998)
Diatoms	-	-	1.1 × 10^5	Reinfelder and Fisher (1991)
Dinoflagellates	-	-	4 × 10^3	Reinfelder and Fisher (1991)
Great Marsh, Delaware	0.01-0.06	0.3-0.7	3 ×10^3 -1 × 10^4	Velinsky and Cutter (1991)
San Francisco Bay-Delta (suspended particulate matter, 1986, 1995, 1996)	0.1-0.4	1-8	1-4 × 10^4	Cutter and cutter (2004) Doblin et al. (2006)
San Francisco Bay Delta sediment	0.1-0.3	0.2 – 0.5	1-5 × 10^3	Johns et al. (1988)
San Pablo Bay (1999)	0.076-0.119	0.318-1.317	2.81× 10^3 – 1.72 ×10^4	This model
Estuary profile (Nov 11, 1999)	0.078-0.212	0.344-1.299	1.77× 10^3 – 2.67 ×10^4	This model

3.3.5 Summary of Model Evaluation

The evaluation process for both short-term (individual sampling dates along the salinity profile) and long-term periods (limited number of fixed locations with multiple years of data) suggests that the model is able to reproduce spatial variation and time trends in several major parameters. Salinity profiles for individual sampling dates, representing different flow conditions, are simulated very well by the model. Evaluation against the long-term record for selected water quality measures suggests seasonal trends in TSM and phytoplankton are

simulated well by the model, although occasional peaks in both parameters are not captured. Model evaluation for selenium concentrations against RMP data for both the short-term and long-term showed that simulated selenium concentrations generally fell within the range of the observed values, although the quality of the fit was not as good as for salinity.

The evaluation against new data under different hydrologic conditions, as shown here, suggests that processes that affect solutes and particulate transport as well sources of phytoplankton, TSM, and selenium are generally well-represented in the model, albeit peak concentrations are not always predicted. The limited ability to capture peak concentrations may be related to the 1-D formulation of the model, which is inherently limited in representing three-dimensional processes.

3.4. PREDICTED SELENIUM CONCENTRATIONS IN BIVALVES, FISH AND BIRDS

Model-predicted selenium concentrations in bivalves (*Corbula amurensis*) for November 11, 1999 were 9.77 ± 4.87 µg/g compared to observed values reported by Stewart et al. (2004; 11 µg/g), using an ingestion rate of 0.45 g/day and assimilation efficiency of 0.20 (elemental), 0.45 (adsorbed selenite) and 0.80 (organic selenide).

Predicted selenium concentrations in *Corbula amurensis* near Carquinez Strait as a function of time were compared to data from Stewart et al. (2004) and are shown in Figure 3-28 for a range of ingestion rates used. Different ingestion rates of particulate selenium by *Corbula amurensis* and assimilation efficiencies for organic selenium were used in the simulation. Predicted ranges in bivalve selenium concentrations are between 2 – 22 µg/g.

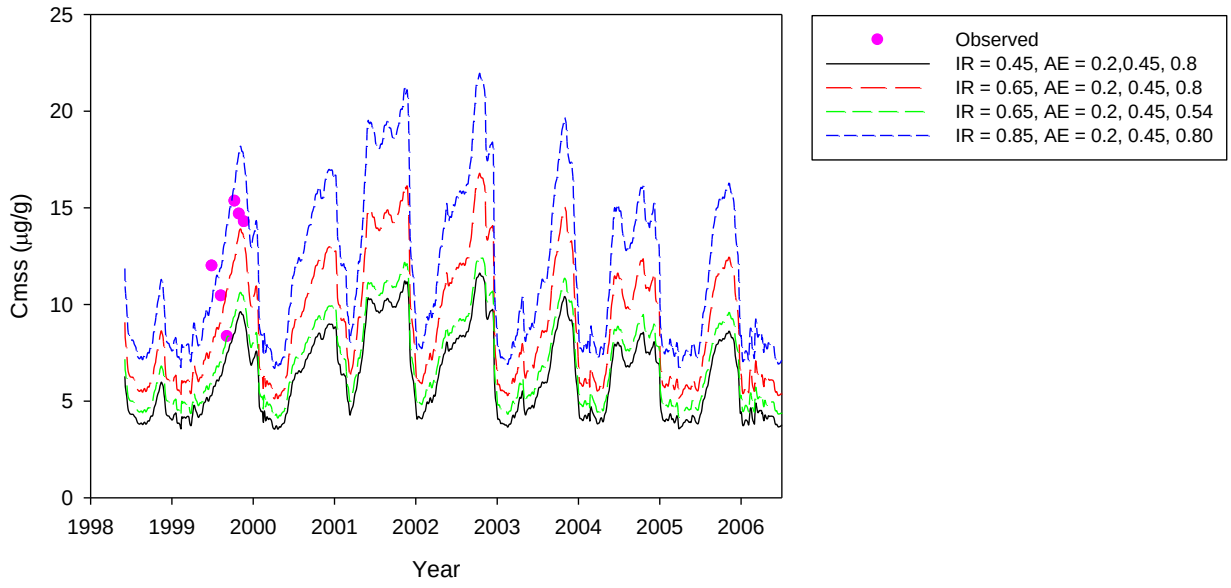


Figure 3-28 **Simulated selenium concentrations in bivalve *Corbula amurensis* near the Carquinez Strait compared to observed values from Stewart et al. (2004; station 8.1). Different AEs in order are for particulate elemental selenium (AE = 0.2), particulate adsorbed selenite and selenate (AE = 0.45), and particulate organic selenium (AE = 0.80), respectively.**

Simulated selenium concentrations in bivalves along the distance of the estuary were also compared to the observed data from USGS for different locations in the Bay during July 1999 to December 1999. The sampling locations by USGS are at stations 6.1, 411 and 415 in Suisun Bay, 8.1 in Carquinez Strait, and 12.5 in San Pablo Bay. The model estimates suggest that selenium concentrations in bivalves increase with the distance from the head of the estuary, although the data are only weakly supportive (Figure 3-29). The data shown are for a fairly limited period and limited spatial extent, and highlight the need for model comparisions with more recent data as well as data at higher salinities (all the way from San Pablo Bay to Golden Gate).

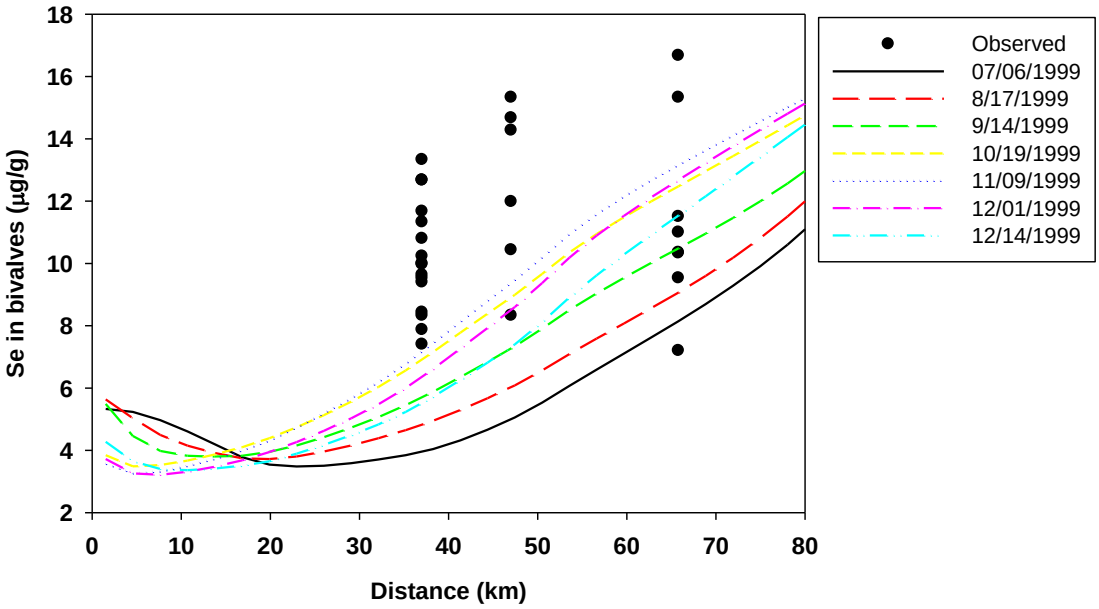


Figure 3-29 **Simulated selenium concentrations in *Corbula amurensis* as a function of distance during sampling dates (using IR = 0.45, AE = 0.20 (for particulate elemental selenium), 0.45 (particulate adsorbed selenite and selenate) and 0.80 (particulate organic selenide)) compared to the observed values.**

The model simulated Se:C ratio in phytoplankton was compared in Figure 3-30 to reported Se:C ratios for several species of phytoplankton, measured under selenite concentrations of 0.15 nM (0.0118 µg/L, concentrations found in NSFB) by Baines et al. (2001). The phytoplankton species *Prorocentrum minimum* is common in San Francisco Bay. Simulated Se:C ratios were also comparable to the mean observed value in the Delta plankton (Baines et al. 2004). This suggests that simulated selenium content in phytoplankton as tracked within the model is in the range of reported data.

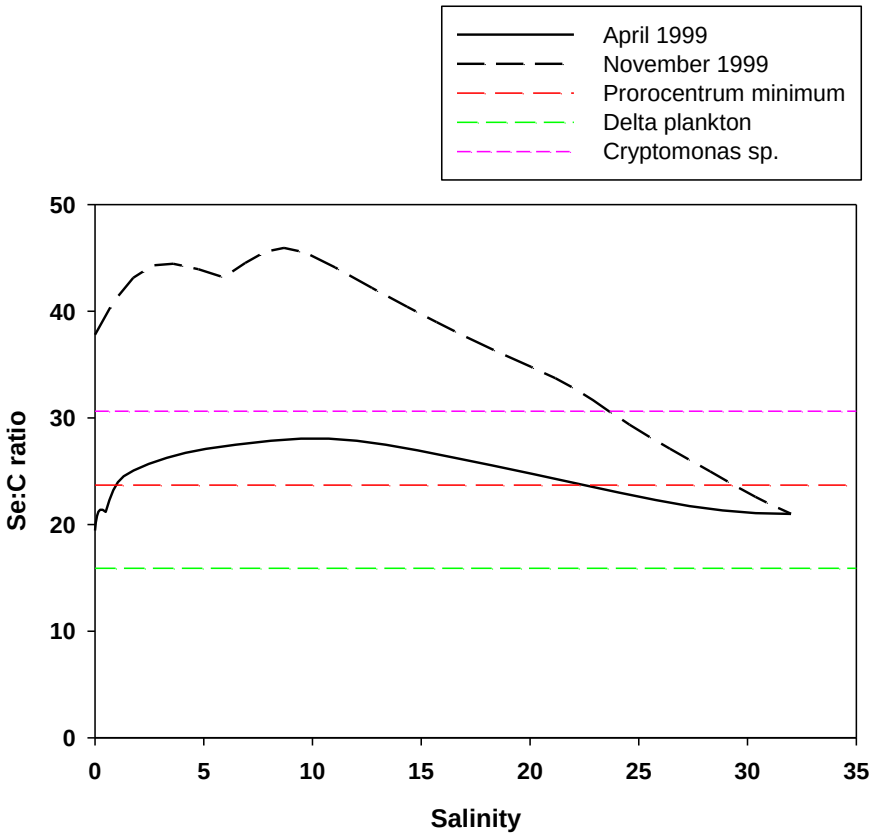


Figure 3-30 **Model simulated Se:C ratio in phytoplankton for April and November 1999 compared to Se:C ratios in *Prorocentrum minimum*, and *Cryptomonas sp*. (measured under 0.15nM selenite by Baines and Fisher 2001) and Se:C ratio in Delta plankton. *P. minimum* and *Cryptomonas sp.* are common species in NSFB.**

Simulated selenium concentrations in bottom sediments were also compared to observed values (Figure 3-31). Estimated selenium concentrations in bottom sediments are generally between 0.18- 0.22 μg/g, slightly lower than observed mean concentration of 0.25 μg/g. The simulated selenium concentrations in sediments show less variation than the observed values. The reason is partly due to the use of a 1-D representation of the sediment bed, and partly due to analytical variability in sediment data.

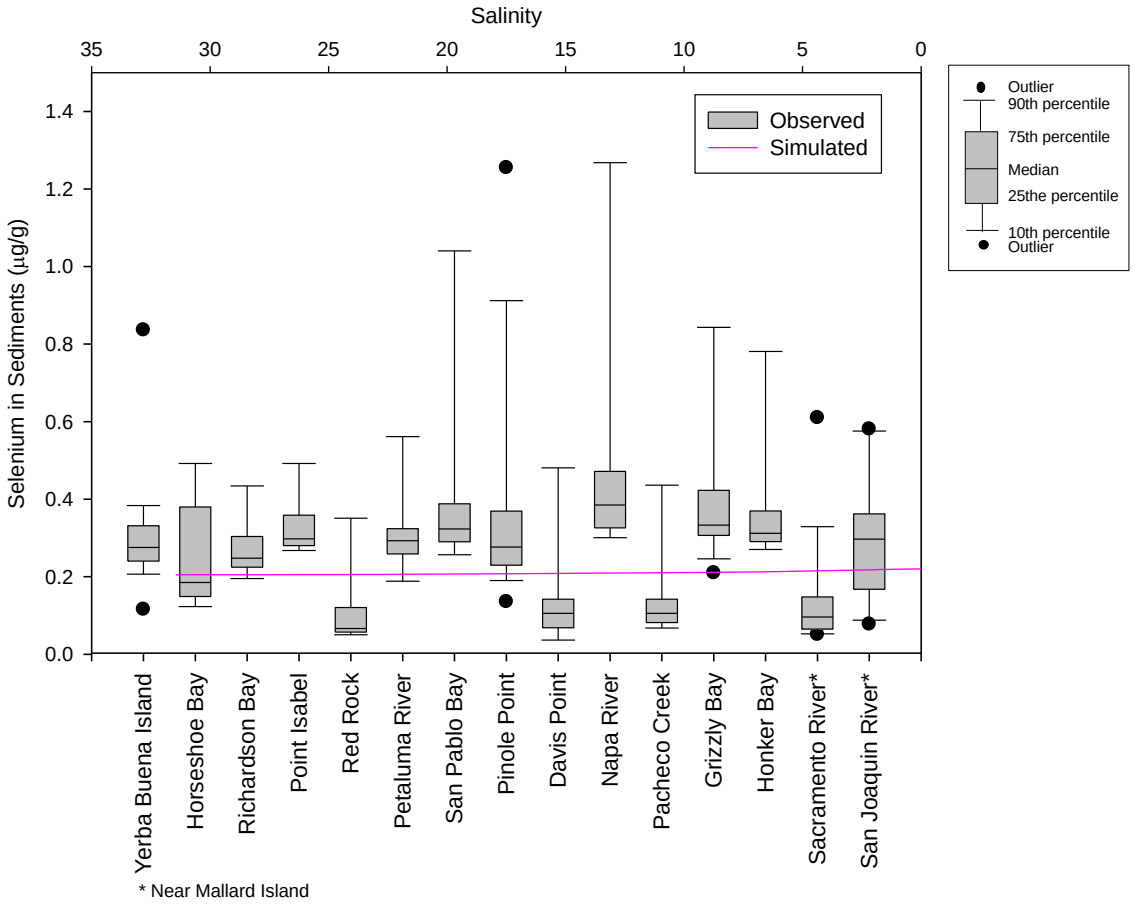


Figure 3-31 Model predicted selenium concentrations in bottom sediments (solid line) compared to observations at different locations, represented as a box plot.

Predicted estuarine-wide selenium concentrations in livers of surf scoter and sturgeon are 186.1 ± 93.9 µg/g and 27.3 ± 16.4 µg/g for November 1999. Predicted mean concentrations in livers of sturgeon compared well with the observed data of 24.1 ± 10.3 µg/g (USGS, unpublished). The selenium concentrations in white sturgeon as presented in TM4 (Tetra Tech, 2008b) are data for 2000-2001 collected at Pittsburg Sturgeon Derby by USGS. White sturgeon sampled from San Francisco Bay-Delta between 1986 and 1990 contained selenium at concentrations ranging from 9 to 30 µg/g dw (mean: 26.55 µg/g) in liver and 7 to 15 µg/g in muscle tissue (mean: 12.57 µg/g; Urquhart and Regalado 1991; White et al. 1988). Lower selenium concentrations in livers of white sturgeon were reported by another study (mean: 9.75 µg/g) between 2002 and 2004 (Linares et al. 2004, cited in Linville, 2006). Predicted selenium concentrations in muscle tissue of white sturgeon are 10.7 µg/g using a trophic transfer factor (TTF) of 1.7. Predicted selenium concentrations in white sturgeon liver and tissue over time compared to the observed data at different locations of the bay (e.g. Suisun Bay, San Pablo Bay, and Carquinez Strait) are shown in Figure 3-32 to Figure 3-34.

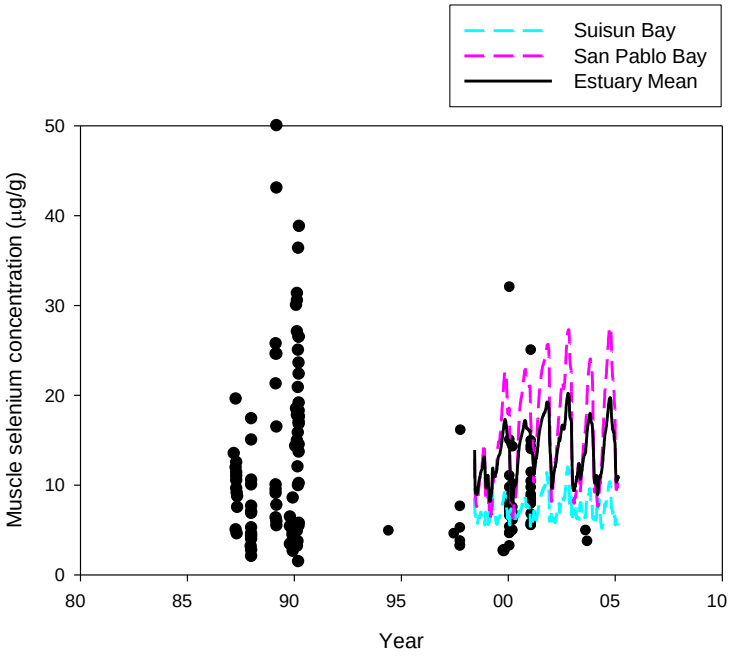


Figure 3-32 **Model predicted selenium concentrations in muscle tissue of white sturgeon at Suisun Bay and San Pablo Bay compared to observed values (White et al., 1988, 1989, Urquhart et al., 1991, USGS and SFEI), using TTF = 1.7.**

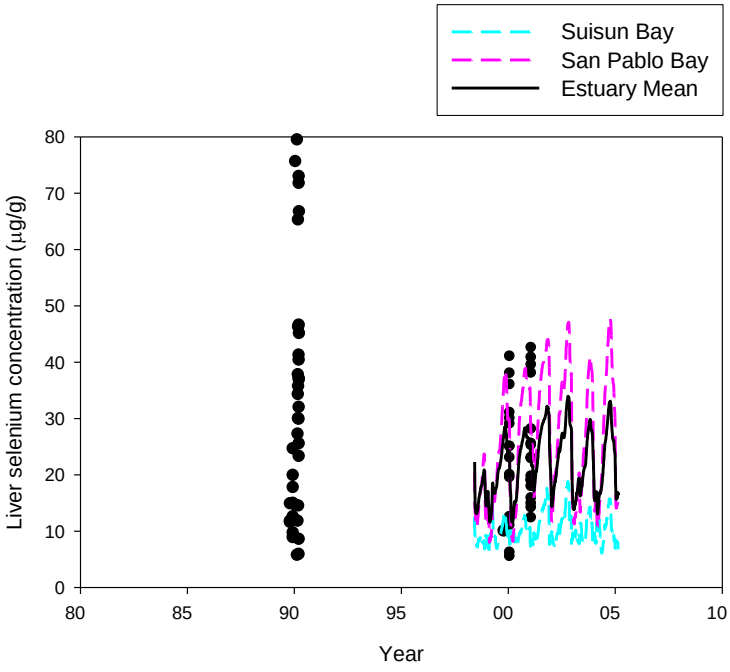


Figure 3-33 **Model predicted selenium concentrations in liver of white sturgeon at Suisun Bay and San Pablo Bay compared to observed values (White et al., 1988, 1989, Urquhart et al., 1991, USGS and SFEI), using Eq. (27).**

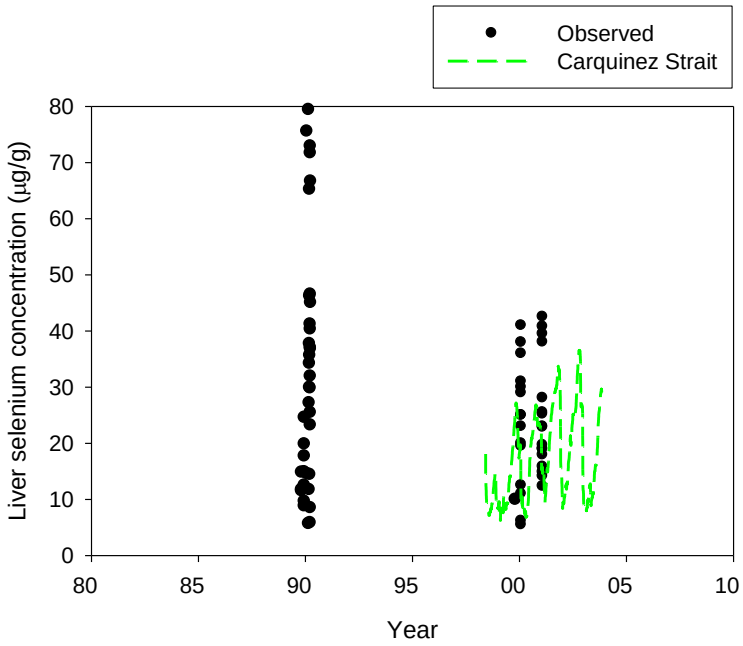


Figure 3-34 **Model predicted selenium concentrations in liver tissue of white sturgeon at Carquinez strait compared to observed values (White et al., 1988, 1989, Urquhart et al., 1991, USGS and SFEI), using Eq. (27).**

Selenium concentrations in muscle tissues of surf scoter and greater scaup are available for the recent years from SFEI (J.Hunt, personal communication). Relationships relating selenium concentrations in bivalves to selenium concentrations in muscle tissues of diving ducks however are only available for *Corbicula* (Presser and Luoma, 2006). With a TTF of 1.8 for scaup, predicted tissue selenium concentrations for scaup are 17.5 µg/g. The predicted concentrations are higher than the observed mean concentration of 12.6 µg/g (J.Hunt, personal communication) in Suisun Bay and San Pablo Bay. Predicted selenium concentrations in muscle tissue by location and time are compared to observed data (Figure 3-40).

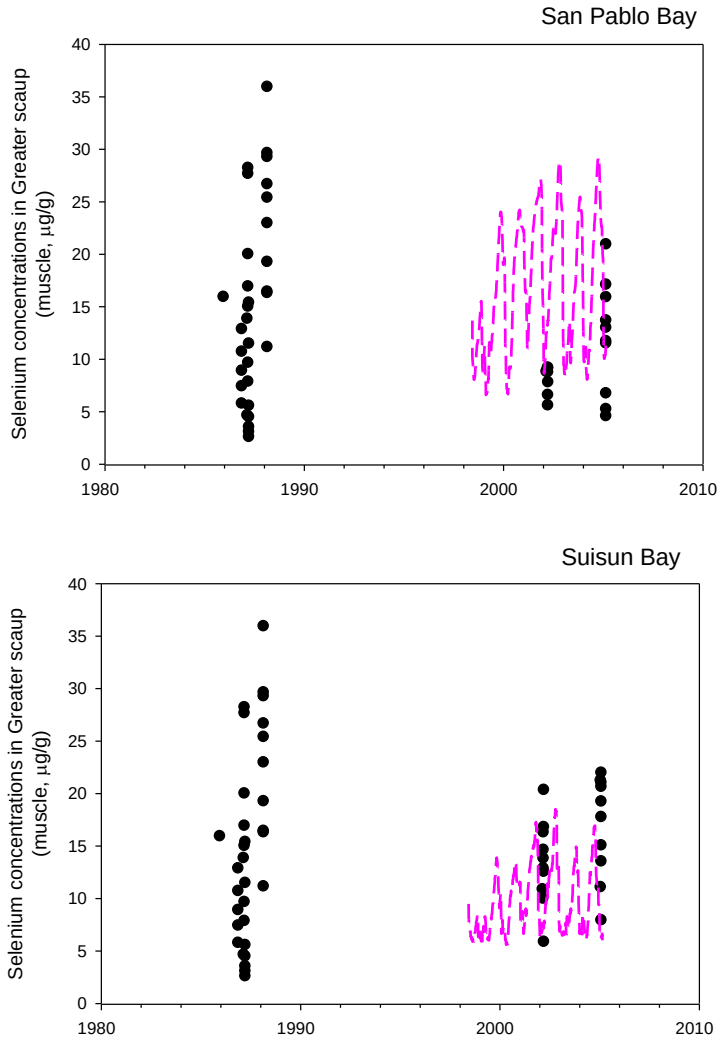


Figure 3-35 **Model predicted selenium concentrations muscle tissue of diving ducks (dry weight; Greater Scaup) compared to observed data in San Pablo Bay and Suisun Bay, respectively (White et al., 1988, 1989; Urquhart et al., 1991; SFEI), using TTF = 1.8.**

HQs for Lesser Scaup, Greater Scaup and Surf Scoter were estimated for three avian species assuming that nearly 100% of their diet consists of clams with concentrations predicted in Figure 3-29. The HQ values are shown in Figure 3-36 and range from less than 1 to about 3, indicating that there is some potential risk to these species at current concentrations. However, because of the conservative nature of the factors in the TRV calculation, the risks are considered to be relatively low.

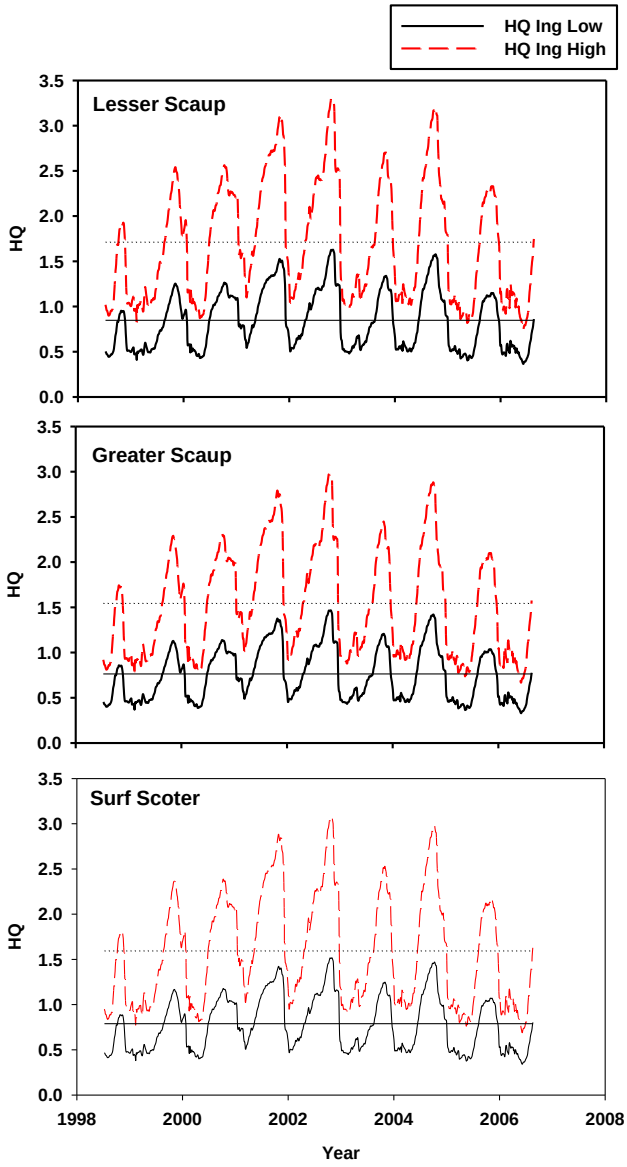


Figure 3-36 **Model predicted hazard quotient for Lesser Scaup, Greater Scaup, and Surf Scoter for low and high ingestion TRVs (threshold reference value). Solid and dashed lines are predicted mean HQ values.**

3.5. MODEL HINDCAST

A model hindcast is another form of evaluation and provides insight on model's capability to simulate conditions that are different from the calibration period in terms of hydrology and internal selenium loading. The calibrated model was run to hindcast selenium concentrations during two time periods prior to refinery clean-up, 1986 and 1998. To simulate selenium concentrations in 1986 and 1998, river discharges from the Sacramento River at Rio Vista and the San Joaquin River at Jersey Point for 1986 and 1998 were used (obtained from IEP). Selenium loads of different species from the refineries for 1986 and 1998 were data from Meseck (2002). Specifically, selenium loads from refineries for these two time periods are listed in Figure 3-6. To run the model for 1998, the simulations were

started on Oct. 1st, 1997. To run the model for 1986 the simulations were started on Oct. 1st, 1985.

Table 3-7
Selenium Loads from Refineries for 1986 and 1998 (after Meseck, 2002).

Refinery	Year	Selenite (kg/d)	Selenate (kg/d)	Organic Selenide (kg/d)	Total Selenium (kg/d)
Chevron	1986	0.66	0.20	0.11	0.98
Valero (Exxon)	1986	0.45	0.11	0.02	0.57
Shell	1986	1.59	0.30	0.08	2.00
Tesoro (Tosco)	1986	0.02	0.11	0.10	0.23
Conoco (Rodeo) Phillips	1986	0.82	0.27	0.11	1.21
Total					4.99
Chevron	1998	0.12	0.20	0.13	0.45
Shell	1998	0.28	0.47	0.32	1.07
Valero (Exxon)	1998	0.28	0.48	0.32	1.09
Tesoro (Tosco)	1998	0.06	0.08	0.06	0.20
Conoco Phillips (Rodeo)	1998	0.28	0.55	0.38	1.22
Total					4.02

Selenium loads from different sources (riverine, refineries, and tributaries) used for the model simulation years (1986, 1998 and 1999 forward) are shown in Figure 3-37. Selenium loads from the rivers show large variation. Water year 1998 shows the highest riverine selenium loads due to high inflows. Selenium loads from refineries show marked decrease from 1998 to 1999. Current selenium loads from refineries are around one-third of the previous loads (prior to refinery clean-up).

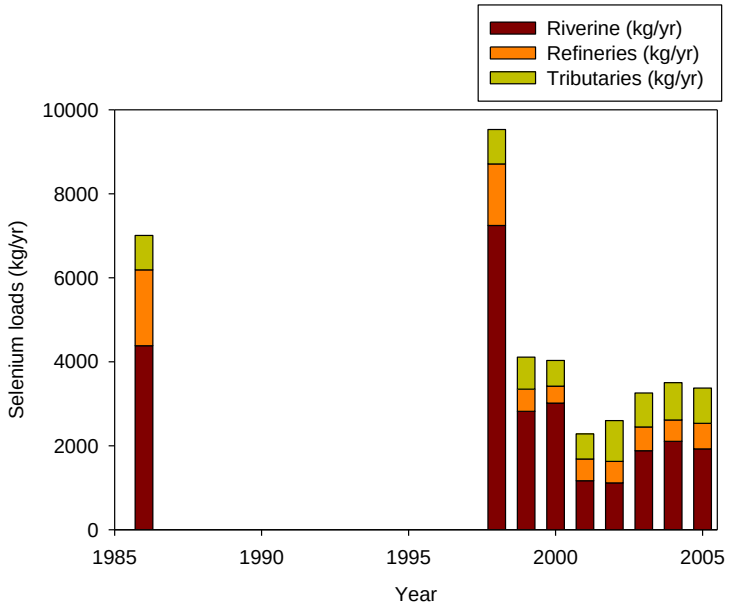


Figure 3-37 **Annual selenium loads from riverine (Sacramento River + San Joaquin), refineries and local tributaries for prior to refinery clean-up (1986 and 1998) and post refinery clean-up (1999-2005) used in the model. Refinery loads for 1986 and 1998 are from Meseck (2002).**

Figure 3-38 to Figure 3-43 show the model hindcast results for 1998. For June (high flow) and October 1998 (low flow), the model-simulated salinity compared well with the observed values. Simulated TSM for October 1998 is able to capture the ETM. Phytoplankton concentrations are simulated well for June 1998 but are over-predicted in October 1998. Model hindcast results for dissolved selenium species for both low and high flow show very good results. The model is able to simulate the relatively conservative mixing behavior of selenite, selenate and organic selenide during high flow (Figure 3-38). For a low flow month (October 1998), it is worth noting that the mid-estuarine peaks in selenite and selenate are simulated well by the model. This indicates that the spatial distribution of selenium inputs from local sources and the transport of dissolved selenium species have been well represented. Spatial patterns in selenite and organic selenide were also captured well by the model (Figure 3-39).

Simulated particulate selenium concentrations compared well with the observed values (Figure 3-40; GOFs = -16.7% to 84.1%). Total dissolved and particulate selenium for June and October 1998 were simulated well by the model (Figure 3-41). Simulated selenium content on particulates for June and October 1998 are very close to the observed values (Figure 3-42). Particularly for the low flow month in October 1998, spatial patterns in particulate selenium were captured well by the model. In some cases, higher particulate elemental selenium and particulate organic selenium concentrations were observed than the simulations. This may be due to in-situ processes of sediment resuspension, which result in higher particulate elemental selenium or variations in phytoplankton concentrations or species that may result in higher particulate organic selenium. These processes are not captured by the model and may explain the differences between observations and simulations in these plots.

The model hindcast for 1986 indicates salinity, TSM and chlorophyll a concentrations are simulated correctly by the model without additional calibration (Figure 3-43). For dissolved selenium, the relatively conservative mixing behavior during high flow (April 1986) and the mid-estuarine peaks during low flow (September 1986) for selenite and selenate are captured well by the model (Figure 3-44). Model-simulated total dissolved and particulate selenium concentrations compared to the observed data are shown in Figure 3-45.

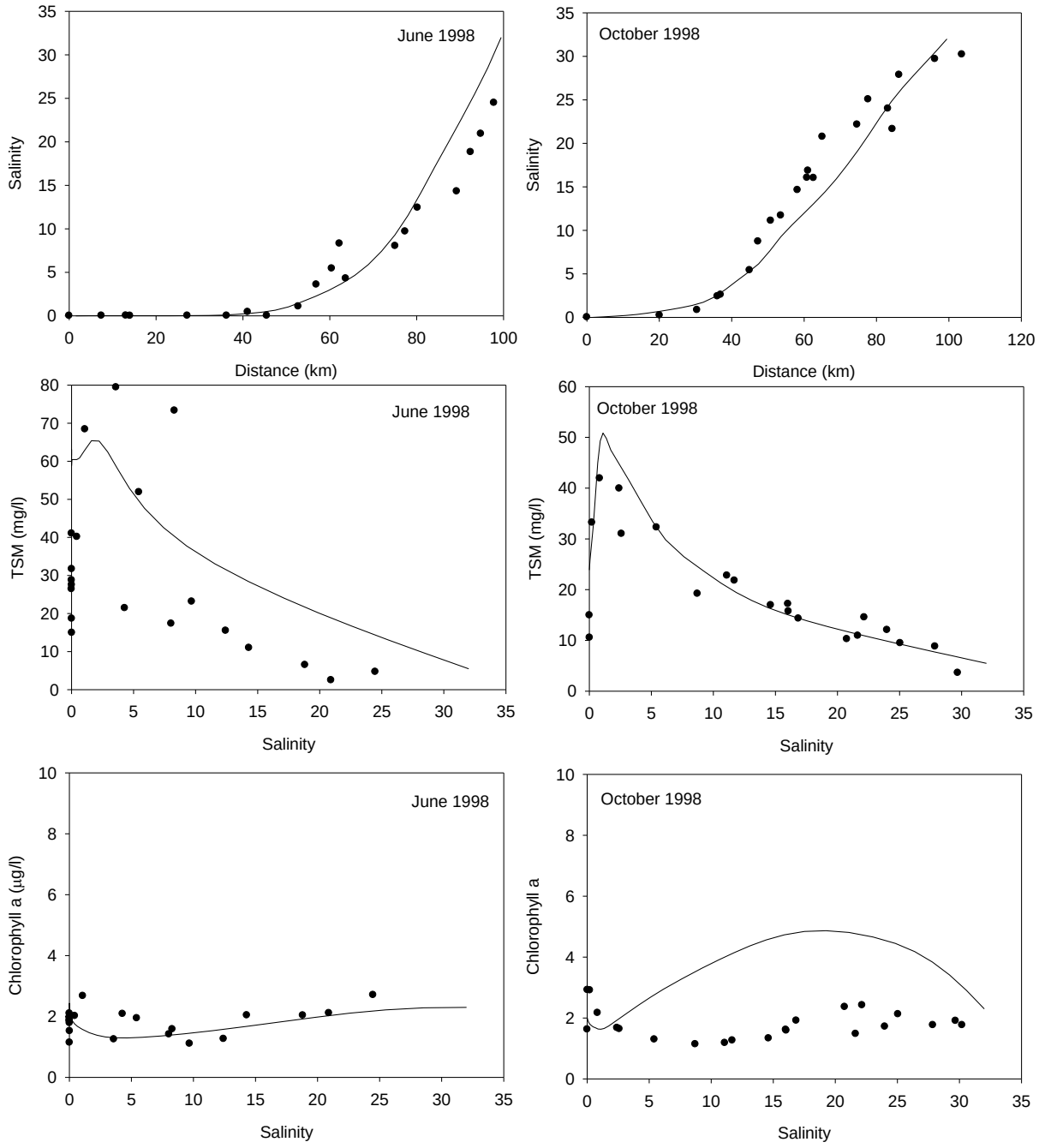


Figure 3-38 Model simulated profiles of salinity, TSM and chlorophyll a compared to observed values for June and October 1998.

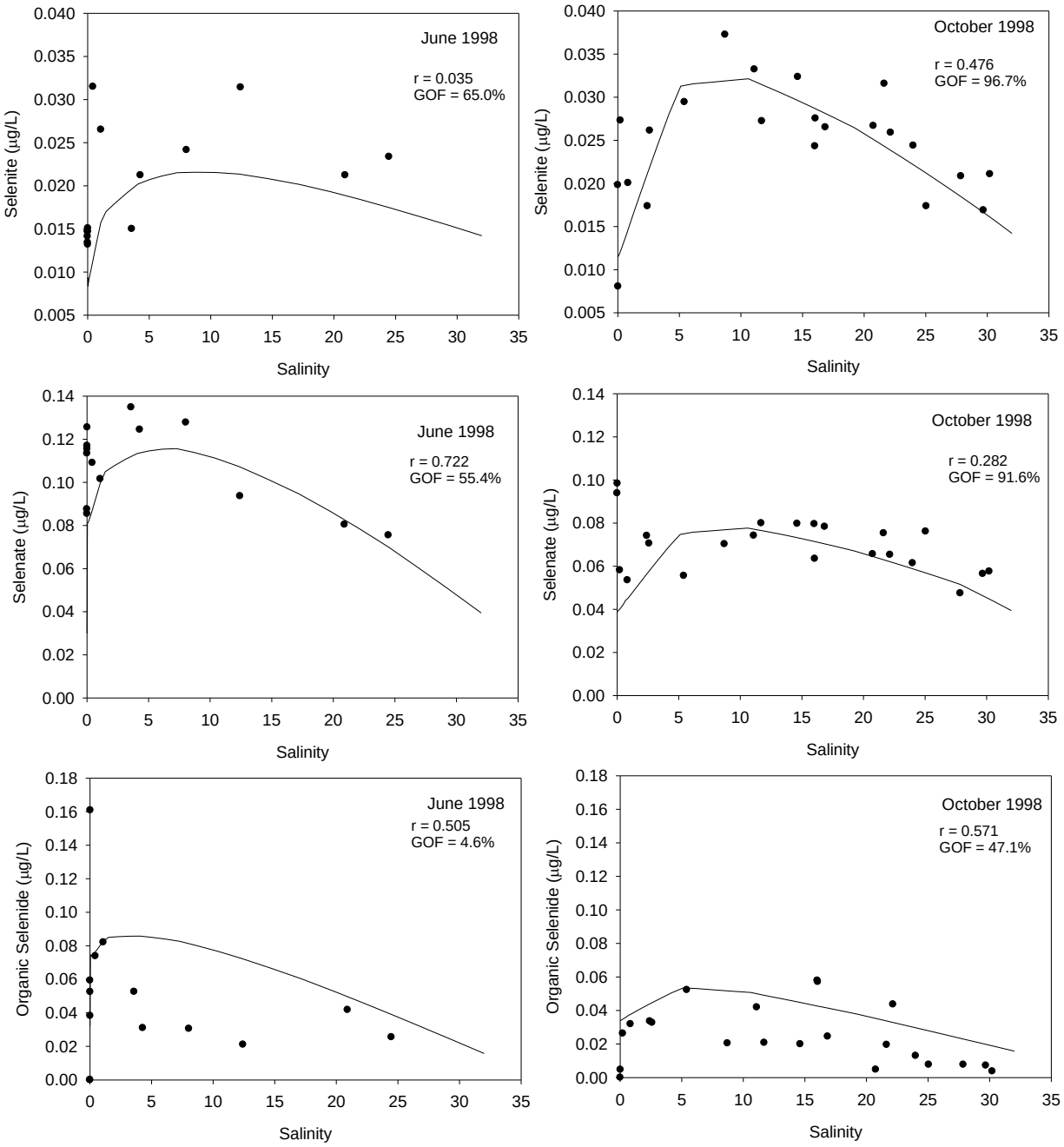


Figure 3-39 Model simulated dissolved selenium by species as a function of salinity compared to observed values for June 1998 and October 1998.

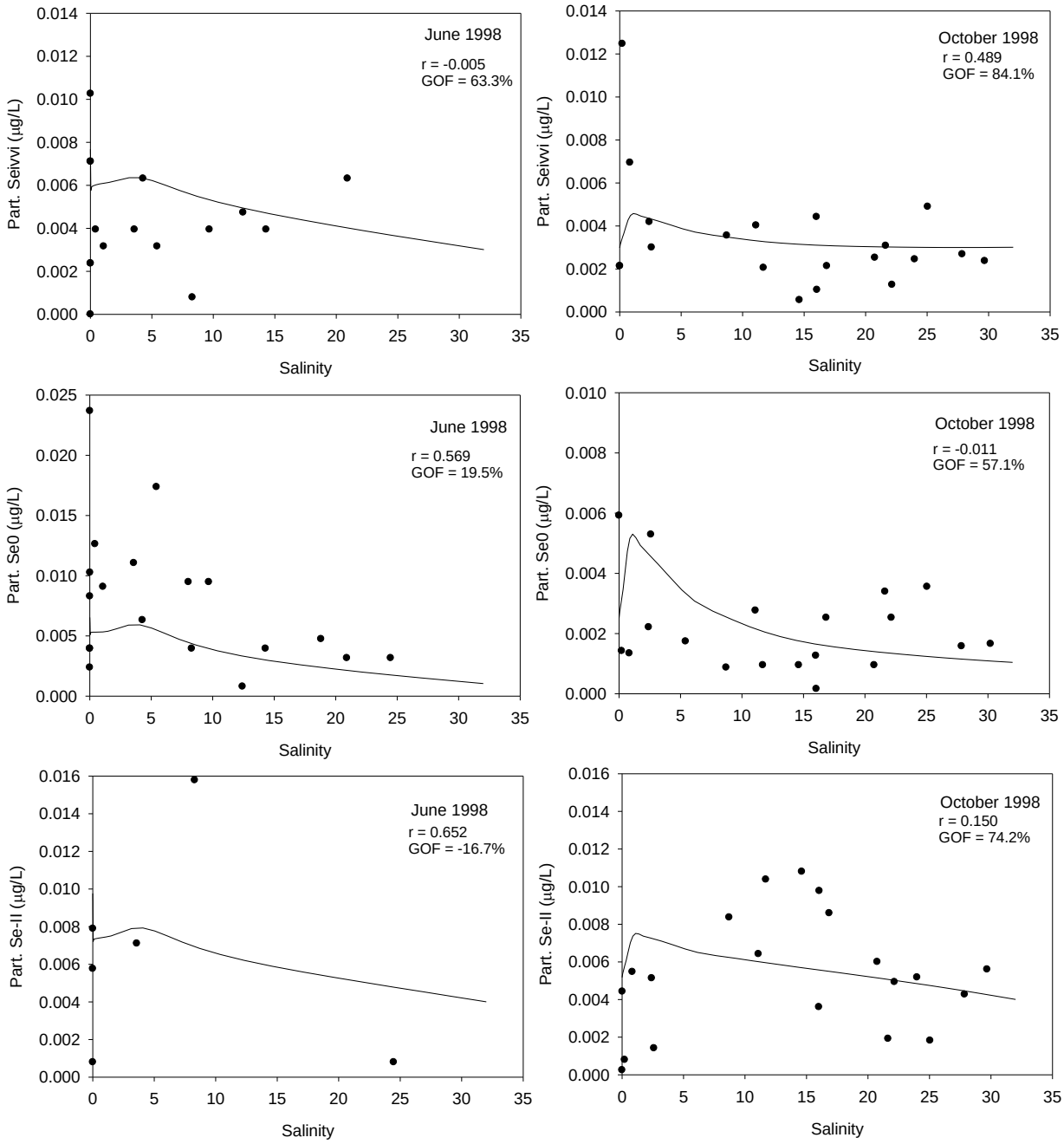


Figure 3-40 Model simulated particulate selenium by species compared to observed values for June 1998 and October 1998.

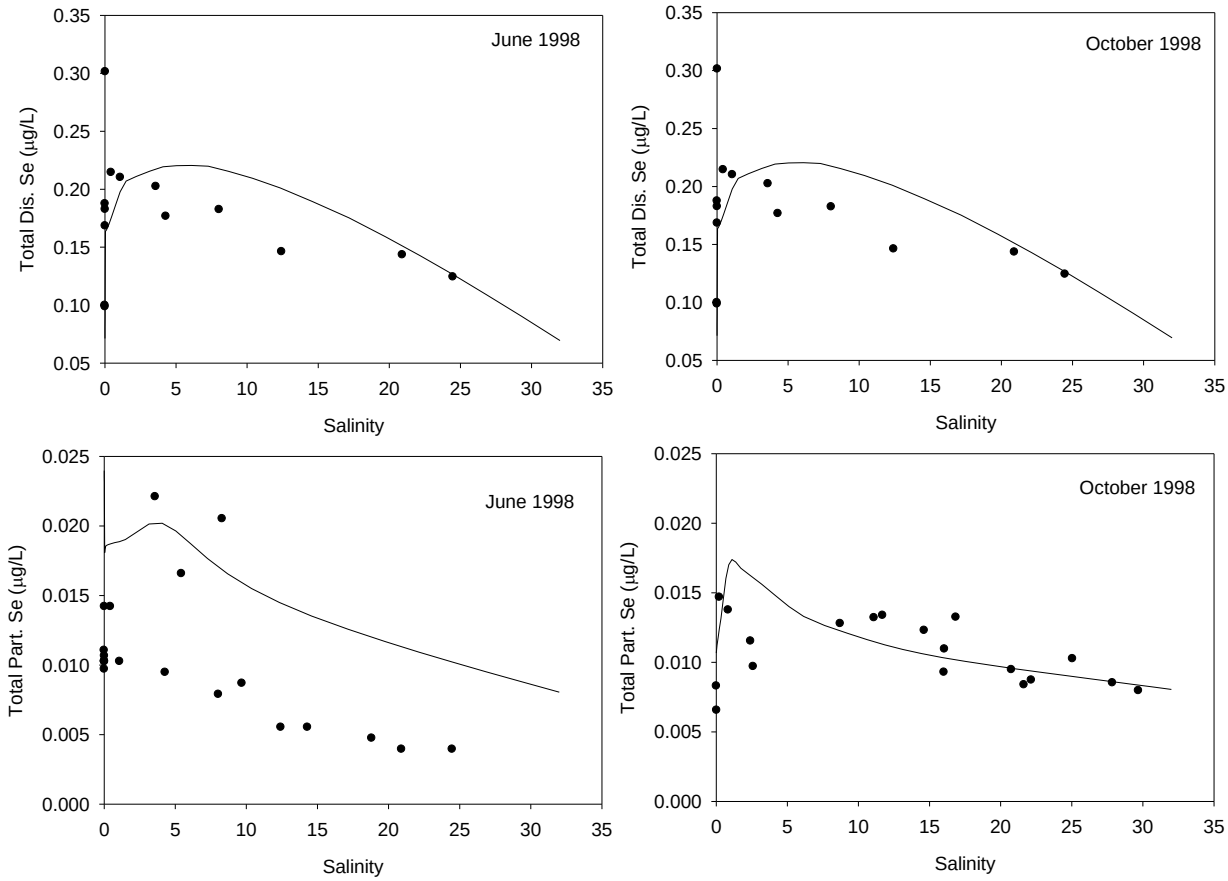


Figure 3-41 **Model simulated total dissolved and particulate selenium compared to observed values for June 1998 and October 1998.**

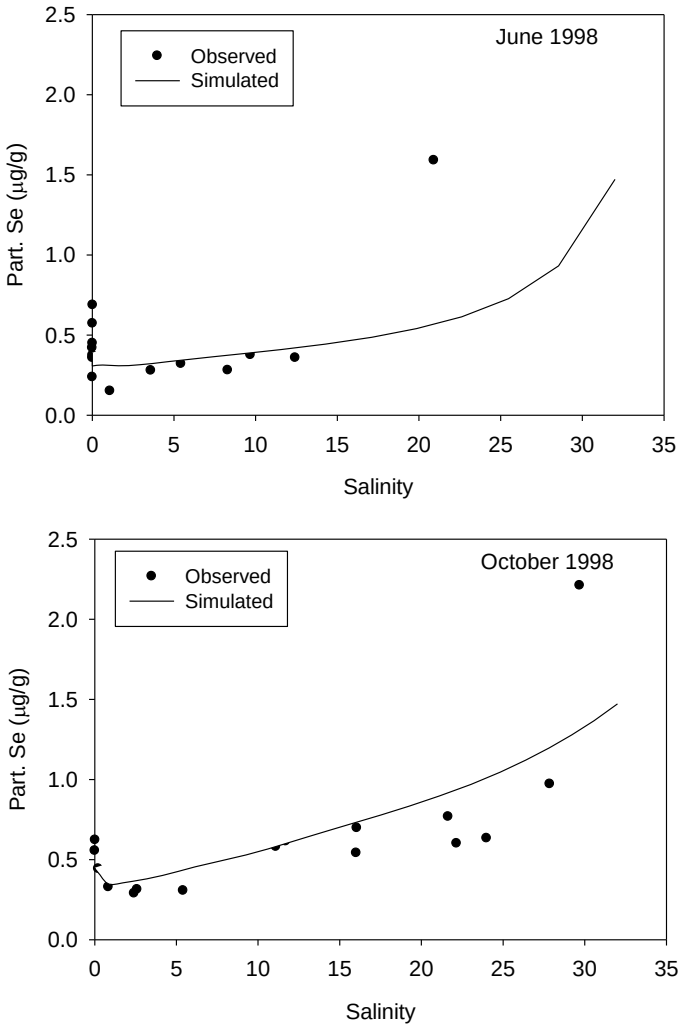


Figure 3-42 Model evaluation of simulated particulate selenium for high flow (June 1998) and low flow (October 1998) in 1998.

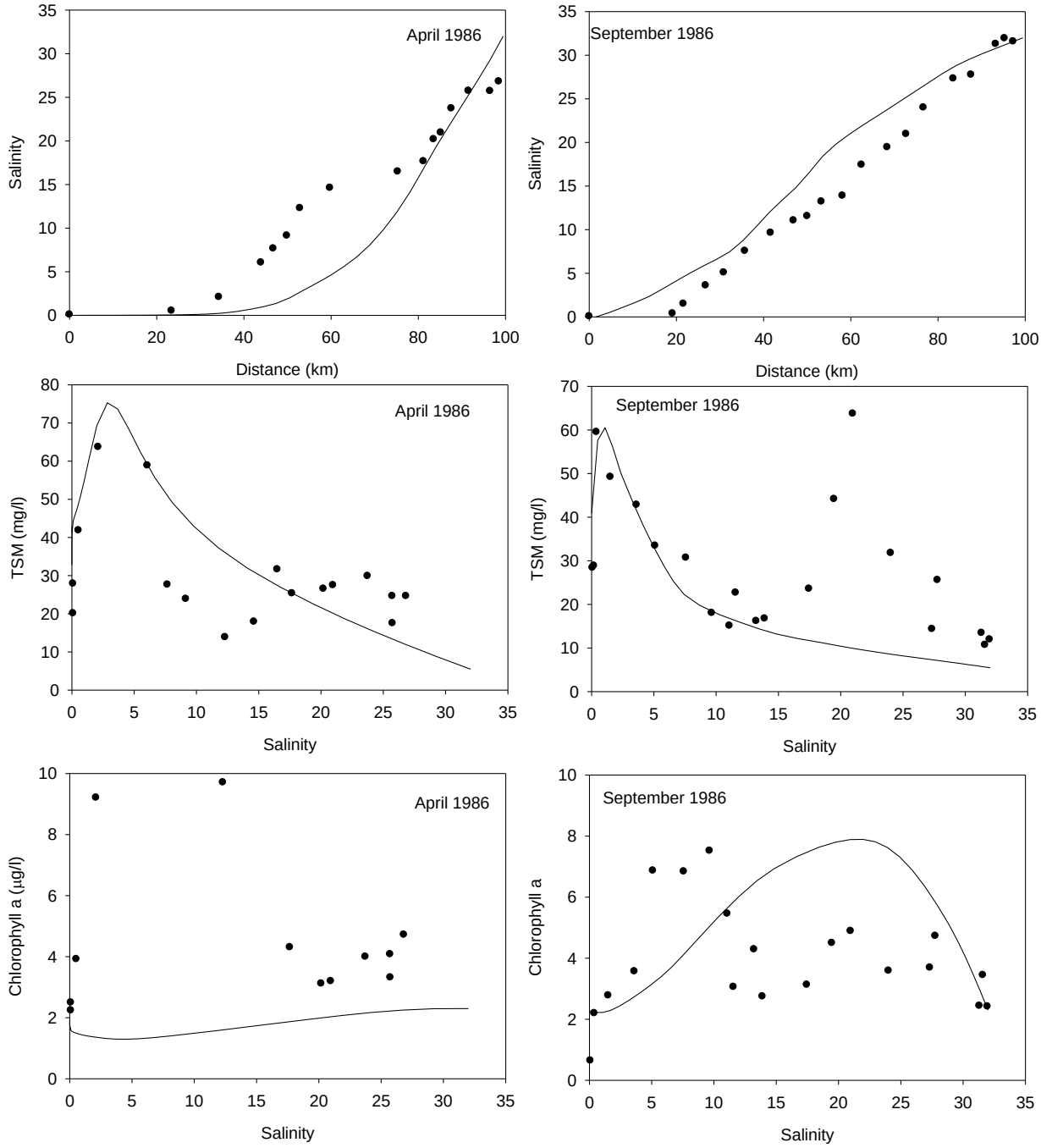


Figure 3-43 Model simulated profiles of salinity, TSM and chlorophyll a compared to observed values for April and September 1986.

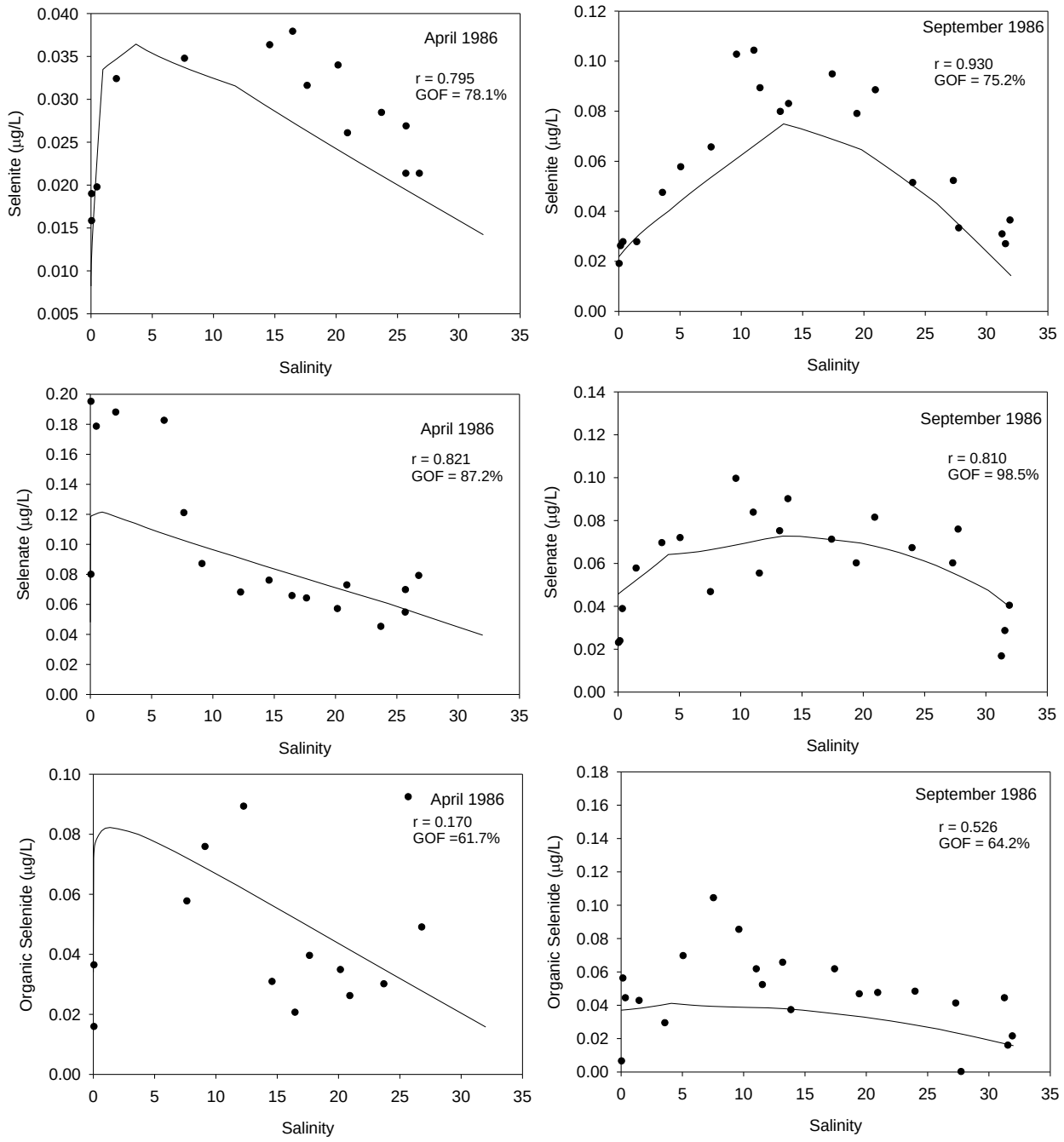


Figure 3-44 Model simulated dissolved selenium by species compared to the observed values for April 1986 and October 1986.

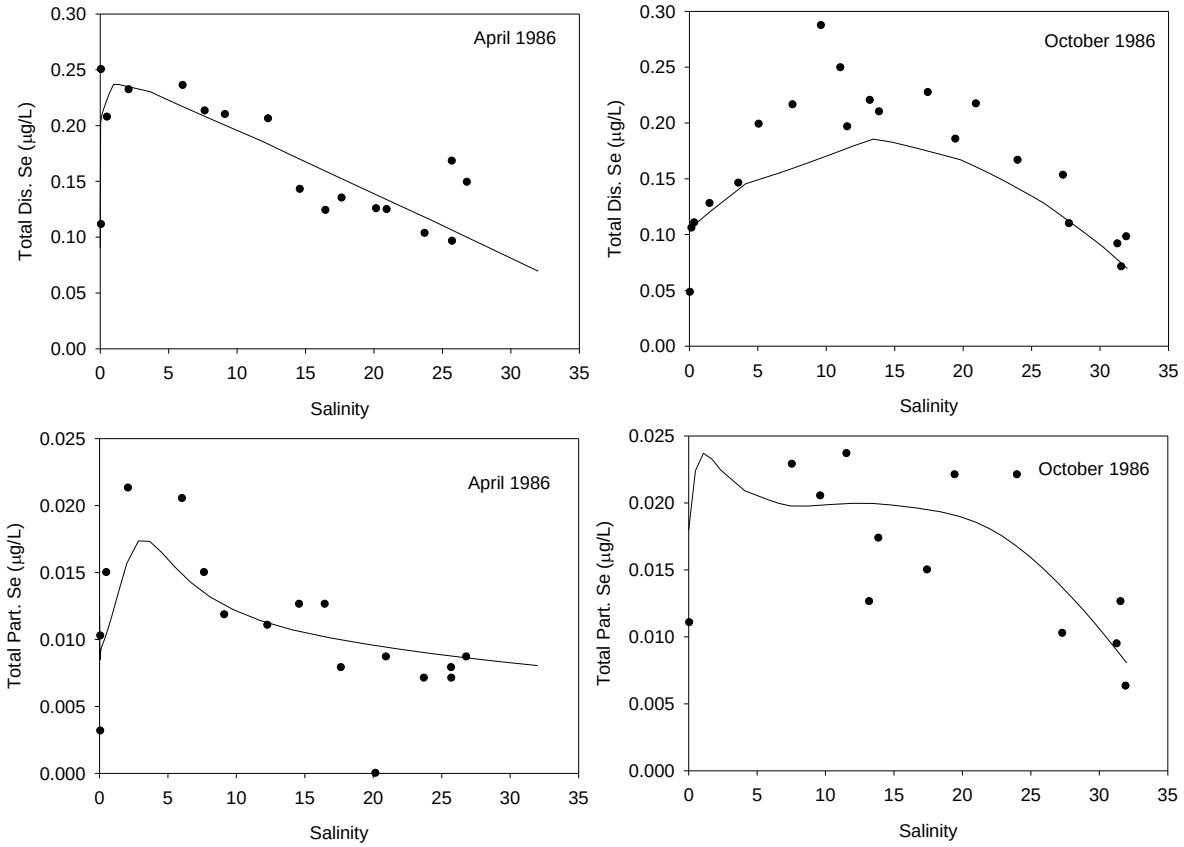


Figure 3-45 Model simulated total dissolved and particulate selenium compared to the observed values for April and October 1986.

3.6. SUMMARY OF MODEL CALIBRATION AND EVALUATION

The extensive database on physical and biological constituents, was complemented with the more limited selenium speciation data, to calibrate the ECoS-NSFB model. In general, salinity was calibrated with greatest precision for all dates. Calibrated fits were poorer for other constituents such as suspended sediments and phytoplankton, likely related to the complexity of factors that influence those constituents. Selenium fits were reasonable, although not as good as salinity. Organic selenium fits were relatively poor, and the large variation in observed data could not be captured by varying the uptake and mineralization rates of organic selenium. This is possibly caused by measurement error in the observed data, or by sources/transformations that have not adequately represented in the model. For all parameters modeled, the model is better able to represent average conditions than spatial and temporal peaks in concentration.

The calibrated model was evaluated against data from other periods. It was found that day-to-day evaluations were not as good as the longer term evaluations for constituents such as phytoplankton and TSM for which such data exist. The selenium values were compared against RMP measurements, and the fits were surprisingly good given the differing source and collection methods of that data set. Model hindcasts, where the currently calibrated model was compared against selenium values from the mid-1980s, were also very good, despite the changes in the source magnitude/speciation and hydrology.

In summary, this effort has demonstrated the ability of the ECoS-based model to represent key features of relevance to selenium fate and transport. In the following section, the calibrated model is tested further under different conditions to better understand its performance, and by extension, the behavior of selenium in NSFB.

4. EXPANDED TESTING AND EXPLORATION OF MODEL PERFORMANCE

Following calibration and evaluation against new data, a series of model runs were conducted to gain more confidence and insight in the model's performance. The goal of the effort was to run the model under different input conditions and with different parameter values to assess the impact to selenium species concentrations. These tests provide insight into the functioning of the model, by identifying processes and variables that are especially sensitive to inputs, or by assessing whether the key variables of interest in this work, e.g., selenium in particulates, are sensitive to other less well-modeled constituents. Another objective of these tests was to evaluate the effect on selenium of parameters where the model fit is not very good, such as phytoplankton. The runs were also used to present summary information, such as mass balances that may be used as a high-level check of the model performance. The runs/testing performed fall into the following seven categories:

- Sensitivity analyses: The calibrated model parameters are perturbed from their base case values to assess whether specific dependent variables respond significantly. Future model development and/or data collection must be targeted at the most sensitive parameters.
- Changing chlorophyll a: The model calibration and evaluation shows that chlorophyll a concentrations were sometimes fit poorly using the ECoS-NSFB framework. The reasons for the poor fit are explored in Section 3, and these additional testing was reported to understand the importance of chlorophyll a variation to the predicted values of particulate selenium.
- Changing uptake rates of dissolved selenium species: The uptake rates for selenate, selenite, and dissolved organic selenide are based on literature reports and calibrated to fit the data. Testing was performed to explore the impact of varying the rates over a wide range, from 10 to 100 times the rates in the base case calibration.
- Different boundary conditions for riverine and seawater input: Particulate selenium concentrations in the riverine and seawater boundary have a significant impact on the concentrations in the bay, and are defined by a small amount of data. A range of values for both boundary conditions was used to evaluate simulated values in the bay.
- Relative contribution of different sources of particulate selenium: Because particulate selenium concentrations are the single most important constituent with respect to bivalve uptake, a more detailed evaluation of the sources (riverine, in-Bay sediment erosion, or phytoplankton) and estuary concentrations is presented.
- Spatial trends in particulate selenium: The model estimates an increase of particulate selenium (in μ/g) with distance across the estuary. The observed data are explored more fully to evaluate the model results of this key constituent for relating to biological uptake.
- Mass balance of selenium: In any modeling effort, a mass balance of inputs and outputs provides a check on the overall numerical representation. Selenium sources, outflows, and changes in stored mass in the water column are presented.

4.1. SENSITIVITY ANALYSIS

A sensitivity analysis was conducted previously by Meseck (2002) for a set of parameters and for various dissolved and particulate selenium concentrations. Under high flow, dissolved selenium concentrations were found to be most sensitive to the riverine inputs. The particulate selenium concentrations were sensitive to parameters that determine riverine inputs of TSM (a, b, c in equation 24), location of estuarine turbidity maximum, photosynthesis rate, and riverine discharge. Under low flow, particulate selenium was generally sensitive to the same set of parameters. In addition, particulate organic selenide was sensitive to selenium uptake rates by phytoplankton, phytoplankton growth rates and selenite oxidation rate.

The sensitivity analysis conducted in this new application of the ECoS framework was for a similar set of selected parameters that affect dissolved and particulate selenium concentrations in the water column. These parameters can be categorized as the Sacramento River and San Joaquin River load inputs (SeVI, SeIV, OrgSe in the Sacramento River and delta removal constants in the San Joaquin Rivers), selenium content on riverine particulates (PSe0, PSeII, and PSeivvi), phytoplankton uptake rates and growth rates (for SeVI, SeIV, SeII), selenite adsorption rate and parameters that determine locations of estuarine turbidity maximum (d in equation 4) and some selenium transformation rates (PSeII mineralization rate k1, partition coefficient for selenite kd). The sensitivity was mainly conducted for a low flow date, November 11 1999. The sensitivity analysis was conducted by altering the parameters for ± 50% and estimating the relative changes in resulted selenium concentrations. The sensitivity is defined as the ratio between the relative changes in resulted parameters to the relative changes in the inputs ($S_{c,k}$) as follows:

$$S_{c,k} = (1 - Cr/Cs)/(1-Kr/Ks) \quad (36)$$

where *Cr* = reference concentrations, *Cs* = simulation result when *Kr* is changed

Kr = reference parameter value, *Ks* is the adjusted parameter value. The variation of ± 50% is approximately the same magnitude of variation as observed in particulate selenium content on riverine particulates and delta selenium load removal constant. When calculating the value of $S_{c,k}$ for each parameter, the model-predicted mean concentrations reference and adjusted parameter conditions were used. Thus, an average value of *Cr* (across the estuary from Rio Vista to Golden Gate) was computed for the reference case, and the average value of *Cs* was computed with the adjusted value of the selected parameter. These were used to calculate $S_{c,k.}$ Note the value of the numerator in equation (36) can take one of two values for the ± 50% change in parameter values (-1 or 0.33).

The results indicate that dissolved and particulate selenium concentrations are most sensitive to riverine input parameters (Table 4-1). Particulate selenium concentrations are sensitive to selenium content on particulate material at the head of the estuary. Dissolved and particulate selenium are less sensitive to selenium transformation coefficients such as phytoplankton uptake and selenite adsorption rates. The model is relatively sensitive to parameters that affect the location and magnitude of the TSM. Particulate organic selenide and particulate selenium are also sensitive to increases in phytoplankton growth rates. The relatively high sensitivity of particulate organic selenium, dissolved selenite and particulate selenium to

increases in phytoplankton growth rate (also as an indicator of phytoplankton concentrations) indicates that certain species of selenium are closely tied to phytoplankton concentrations. In addition, particulate organic selenide is also sensitive to its mineralization rate (k_1).

Figure 4-1 shows the sensitivity of dissolved selenium (selenate, selenite and organic selenide) to changes in riverine input. Overall, dissolved selenium is very sensitive to changes in riverine inputs. The effects are most significant at the head of the estuary, and due to mixing with seawater, which is defined by boundary conditions for various constituents such as salinity, selenium, phytoplankton, etc., the effects become smaller with transport distance along the estuary. Particulate selenium (adsorbed selenite and selenate, particulate organic selenide, and particulate elemental selenium, expressed as μg/L) is also sensitive to changes in riverine inputs (Figure 4-2). Sensitivity of particulate organic selenide concentrations to phytoplankton growth rate, mineralization rate, selenium content in phytoplankton in the riverine and seawater endmembers, scaling factors of Ubeps and Kbeps are shown in Figure 4-3 to 4-4.

Model simulated particulate selenium concentration (in μg/g) is sensitive to parameter used in specifying riverine TSM concentration as a function of flow (Figure 4-5a). In simulating particulate selenium concentrations, selenium concentration in phytoplankton in seawater and riverine end members are important parameters. Particulate selenium concentrations are relatively sensitive to seawater endmember phytoplankton selenium concentration and not very sensitive to riverine phytoplankton selenium (Figure 4-5b, c).

Table 4-1
Sensitivity Analysis for Changing Parameters by 50% During Low Flow (Nov. 1999).
|Sc,k| < 0.15 is Insensitive.

	Org.Se	SeVI	SeIV	P Org Se	P Seivvi	PSe0	Part. Se (ug/g)
SeVI SacRiv (+50%)		0.418	0.006	0.024	0.004		0.010
SeVI SacRiv (-50%)		0.195	-0.002	0.008	-0.001		0.003
SeIV SacRiv (+50%)			0.244	0.021	0.002		0.009
SeIV SacRiv (-50%)			0.097	0.007	0.001		0.003
OrgSe SacRiv (+50%)	0.399		0.084	0.029			0.012
OrgSe SacRiv (-50%)	0.181		0.030	0.010			0.004
SeVI SJR input (+50%) Delta Removal Constant)		0.020		0.001			0.001
SeVI SJR input (-50%) (Delta Removal Constant)		0.007					
SeIV SJR input (+50%) (Delta Removal Constant)			0.000				
SeIV SJR input (-50%) (Delta Removal Constant)			0.001				
SeII SJR input (+50%) (Delta Removal Constant)	0.034		0.007	0.003			0.001
SeII SJR input (-50%) (Delta Removal Constant)	0.012		0.002	0.001			
Riverine PSe0 (+50%)						0.269	0.044
Riverine PSe0 (-50%)						0.109	0.015
Riverine PSeII (+50%)	-0.004		-0.001	0.214			0.081
Riverine PSeII (-50%)	0.002			0.061			0.019
Riverine Pseivvi (+50%)					0.304		0.071
Riverine Pseivvi (-50%)					0.127		0.025
Refinery SeIV (-50%)			0.026	0.010			0.004
Refinery SeIV (+50%)			0.073	0.003			0.001
SeVI uptake rate (+50%)	0.002	-0.006	-0.006	0.063			0.029
SeVI uptake rate (-50%)	0.001	-0.002	-0.002	0.022			0.010
SeIV uptake rate (+50%)	0.003		-0.029	0.089			0.042
SeIV uptake rate (-50%)	0.001		-0.010	0.032			0.015
SeII uptake rate (+50%)	-0.011		-0.002	0.058			0.027
SeII uptake rate (-50%)	-0.004		-0.001	0.020			0.009
Selenite adsorption rate (+50%)							
Selenite adsorption rate (-50%)					0.001		
Phytoplankton growth rate (+50%)	0.047	0.062	0.245	-0.617			-0.295
Phytoplankton growth rate (-50%)	-0.002	-0.002	-0.011	0.085	-0.015		0.023
PSeII mineralization rate k1 (+50%)	0.030			-0.161			-0.070
PSeII mineralization rate k1 (-50%)	0.012			-0.055			-0.025
Partition coefficient kd (+50%)	-0.004	-0.002	0.005		0.006		0.001
Partition coefficient kd (-50%)	0.001	0.001	-0.002		0.002		0.001
Adsorption rate a (+50%)	-0.004	-0.002	0.005		0.008		0.001
Adsorption rate a (-50%)	0.001	0.001	-0.002		-0.001		0.000
Sacramento River Discharge (+50%)	-0.026	-0.039	-0.244	0.032	0.323		-0.269
Sacramento River Discharge (-50%)	-0.030	-0.018	-0.050	-0.331	0.120		-0.241
Phytoplankton Se in seawater (+50%)	0.012		0.001	0.395			0.297
Phytoplankton Se in seawater (-50%)	0.004		0.000	0.179			0.123
Riverine phytoplankton Se (+ 50%)	0.054	0.040	0.032	0.039	0.187	0.031	0.018
Riverine phytoplankton Se (-50%)	-0.018	-0.007	-0.011	-0.012	0.047	-0.010	-0.006
Scaling factor for Ubeps (+50%)	-0.001		0.012	0.645	0.706	1.539	-0.162
Scaling factor for Ubeps (-50%)	0.003	0.002	0.003	0.071	0.112	0.558	-0.101
Scaling factor for Kbeps (+50%)	-0.008	-0.006	-0.011	-0.180	-0.318	-1.543	0.305
Scaling factor for Kbeps (-50%)	-0.001		-0.005	-0.408	-0.437	-0.725	0.084
c (factor relates freshwater discharge and sediment input +50%)	0.372	0.011	0.113	3.033	3.783	4.157	-2.559
c (factor relates freshwater discharge and sediment input - 50%)	0.036	0.070	0.302	-0.962	1.451	2.865	-1.135
Dispersion coefficient (Kw) (+50%)	-0.148	-0.181	-0.108	0.080	0.134	0.418	0.023
Dispersion coefficient (Kw) (-50%)	-0.074	-0.086	-0.059	0.038	0.036	0.196	0.067

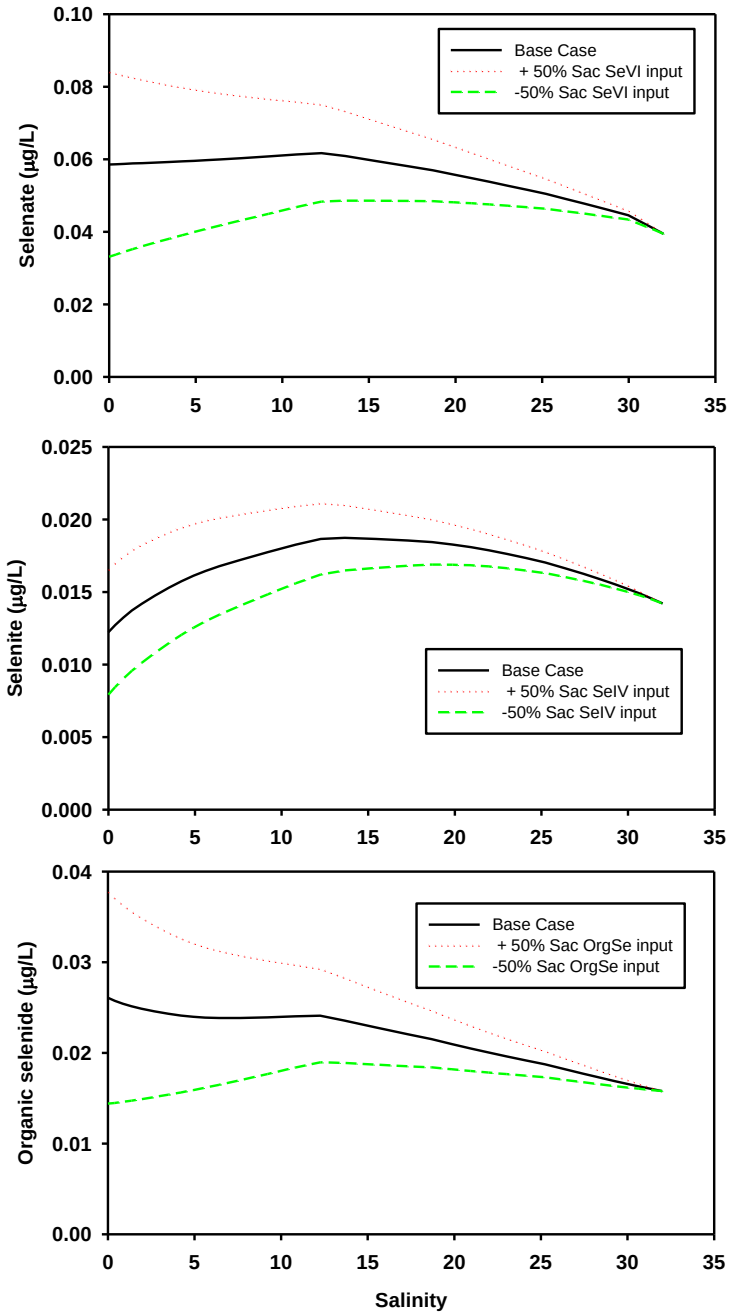


Figure 4-1 **Model sensitivity of dissolved selenate, selenite and organic selenide concentrations during low flow to riverine inputs. Note the convergence of the plots at the seawater boundary in this and subsequent plots. This is a reflection of the boundary condition used in the model.**

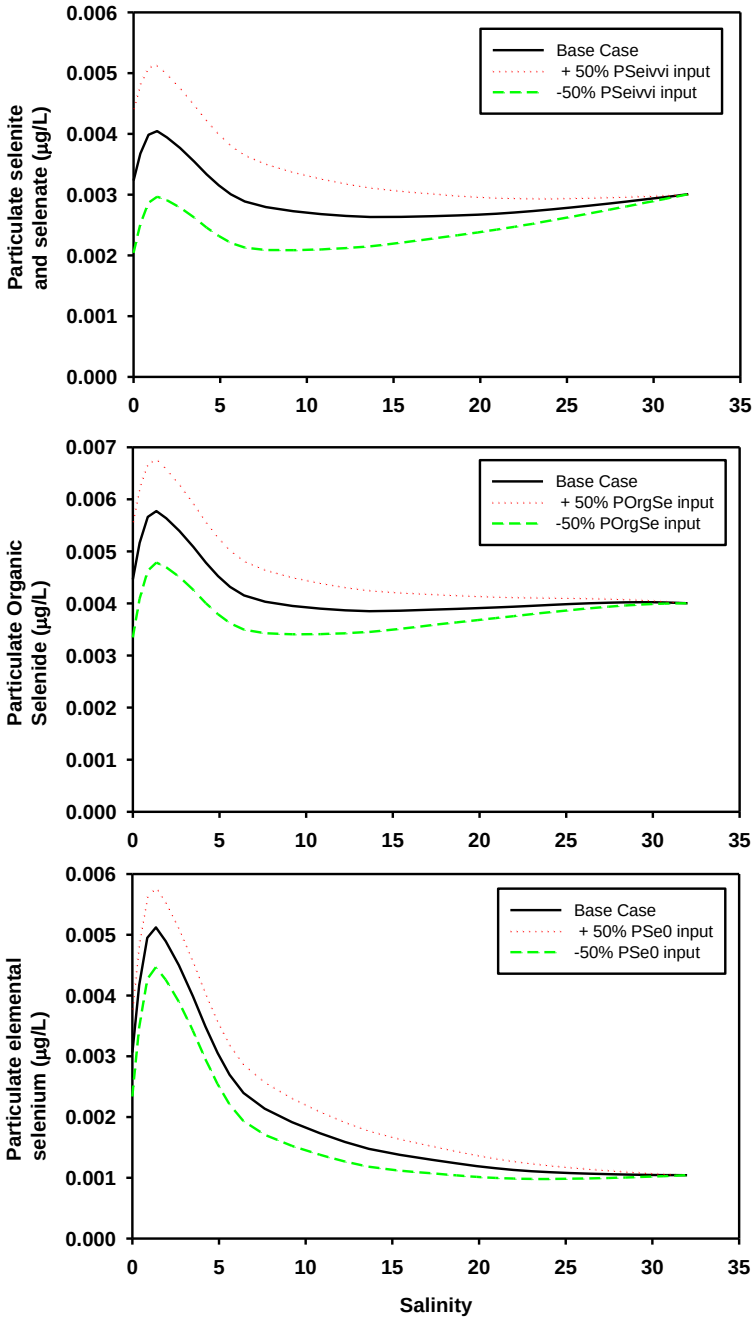


Figure 4-2 **Model sensitivity of particulate adsorbed selenite + selenate, particulate organic selenide and particulate elemental selenium during low flow in response to changes in riverine inputs**

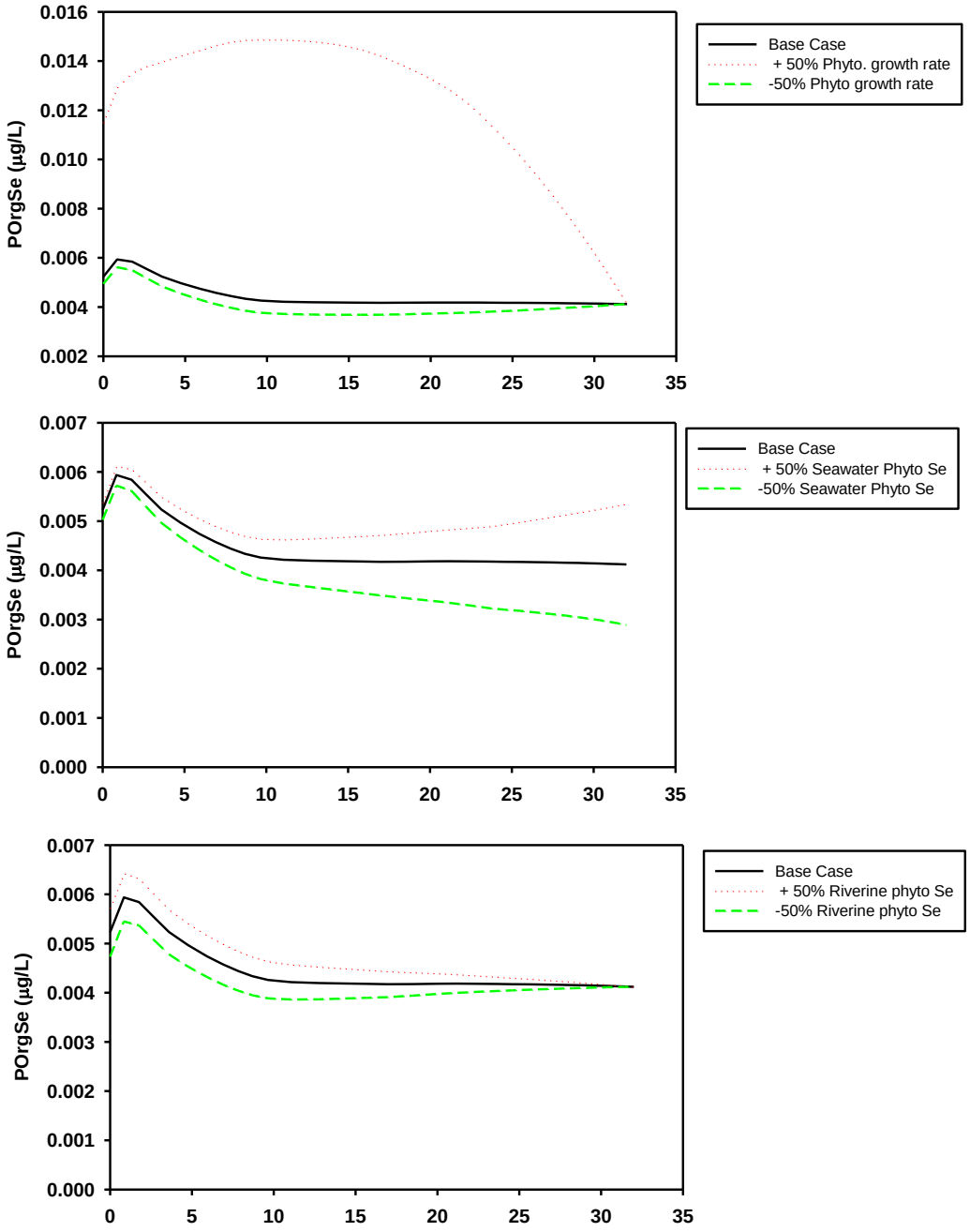


Figure 4-3 **Modeled sensitivity of particulate organic selenide in low flow to changes in: a) phytoplankton growth rate, b) seawater phytoplankton selenium, and c) riverine phytoplankton selenium.**

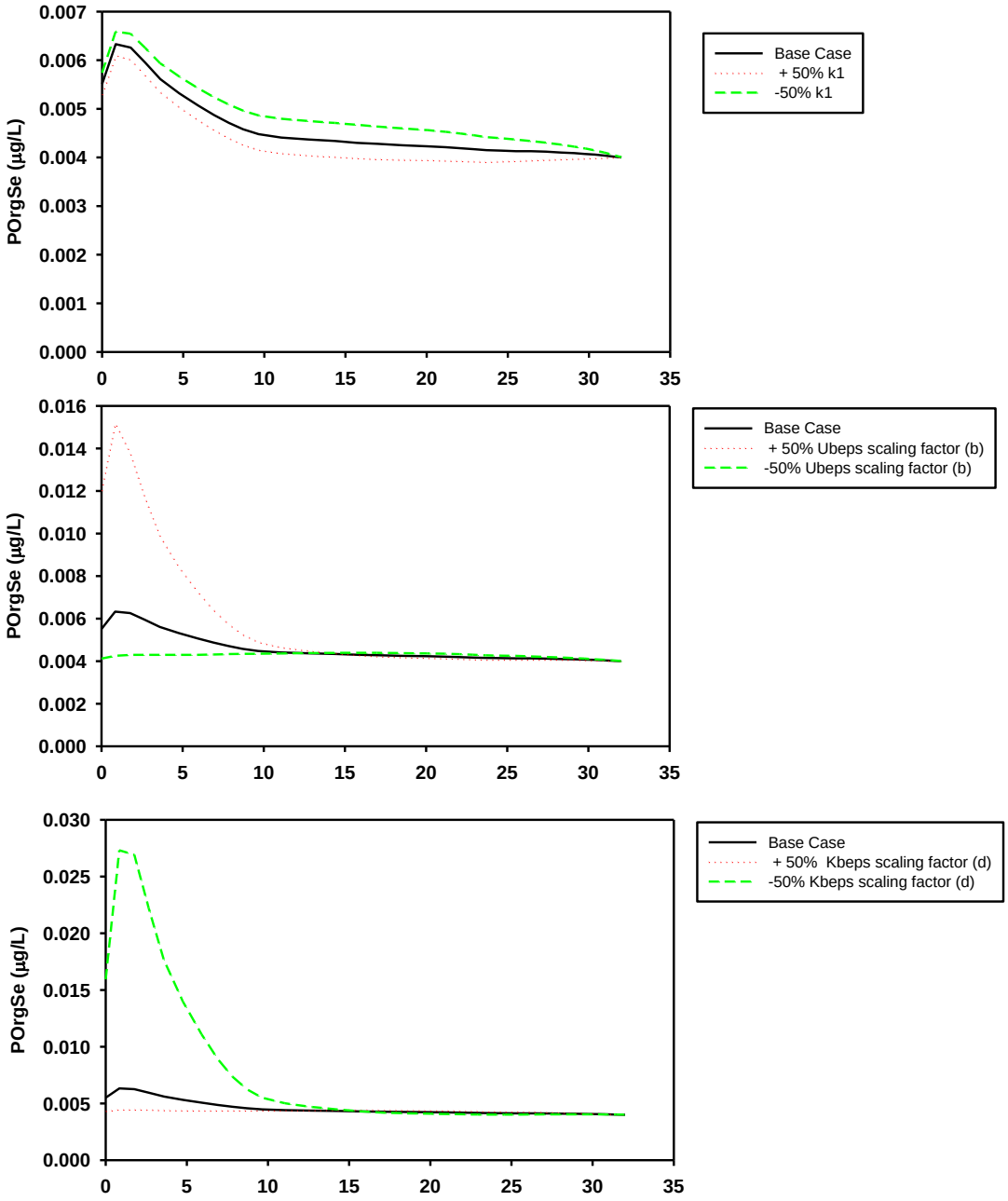


Figure 4-4 **Modeled sensitivity of particulate organic selenide in low flow to changes in: a) mineralization rate k1, b) scaling factor in Ubeps (b), and c) scaling factor in Kbeps (d).**

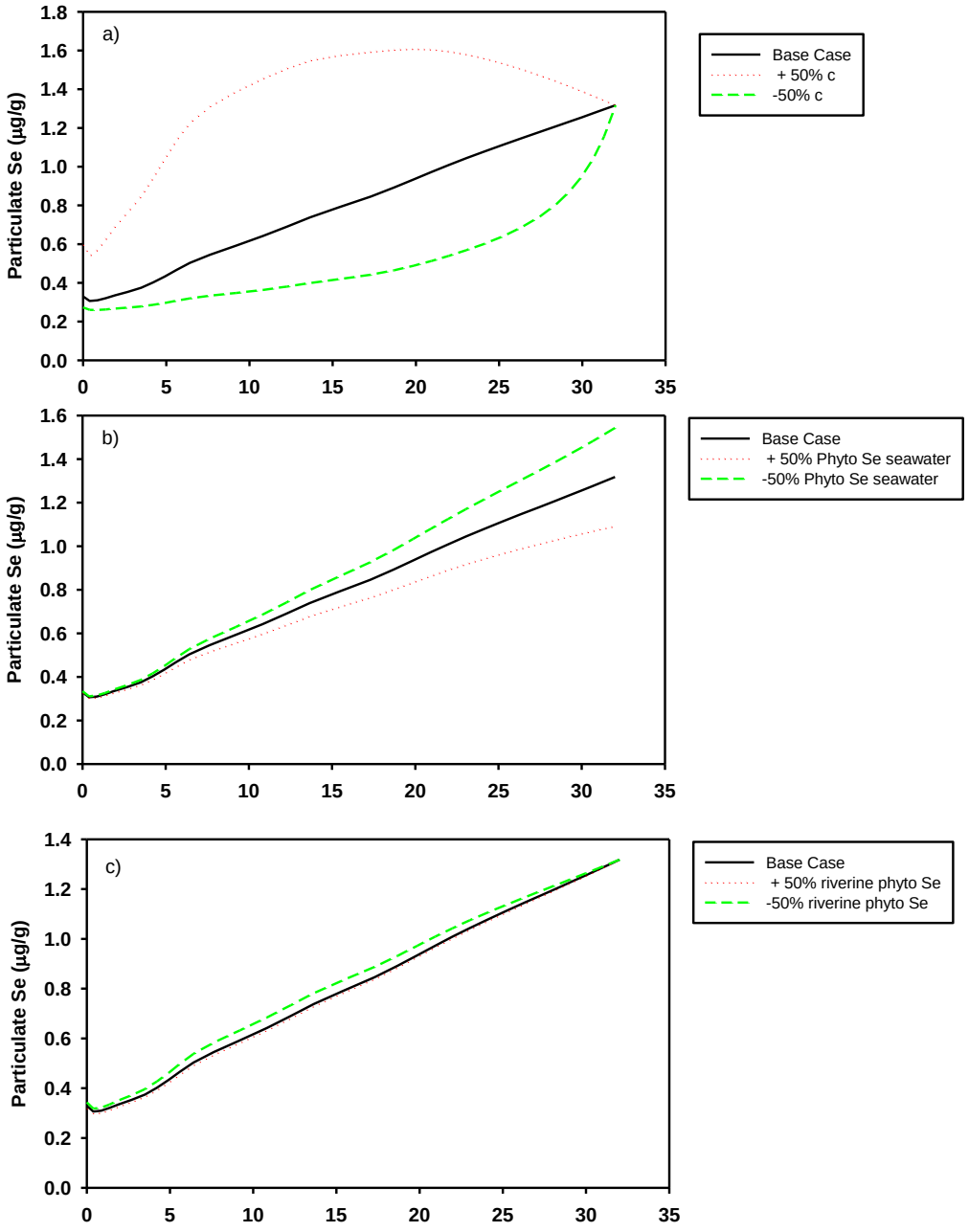


Figure 4-5 **Modeled sensitivity of particulate selenium to changes in a) parameter c (factor that relate TSM concentration with flow), b) phytoplankton selenium in seawater and c) riverine phytoplankton selenium.**

Of all the factors evaluated in this section, the sensitivity analysis highlights the need for detailed characterization of sources, including selenium speciation, to better capture conditions in the estuary. Although selenium speciation data have been reported for some time periods (Cutter and Cutter, 2004; Doblin et al., 2006), the vast majority of the data collection is in terms of total or dissolved selenium.

4.2. CHANGING CHLOROPHYLL A

The uptake of selenium by phytoplankton plays an important role in selenium transformation from the dissolved phase to the particulate phase. Some studies have shown possible increases in phytoplankton concentrations in the North San Francisco Bay in recent years (Cloern et al., 2007). A potential consequence of the increases in phytoplankton concentrations is an increase in particulate selenium concentrations (expressed in units of µg/g). The sensitivity of simulated particulate selenium concentrations (in µg/g) to increases in phytoplankton concentrations during low flow was tested through multiplying observed chlorophyll a concentrations in November 1999 (approximately 2 µg/L) by a factor of 5, 10, and 15 (which result in average chlorophyll a concentrations approximating 10, 20 and 30 µg/L). Model simulated selenium content on particulates can be as high as 1.2, 1.6 and 2.0 µg/g for chlorophyll a concentrations of 10, 20 and 30 µg/L (Figure 4-6). Mean selenium concentrations on particulates along the estuary was at 0.79, 0.94, 1.12, and 1.29 µg/g under chlorophyll a concentrations of 2, 10, 20, and 30 µg/L, respectively. With the increase of chlorophyll a concentrations from 2 µg/L to 10, 20 and 30 µg/L, estuarine mean selenium concentrations on particulates increased by 19.7%, 42.5% and 63.8%, respectively.

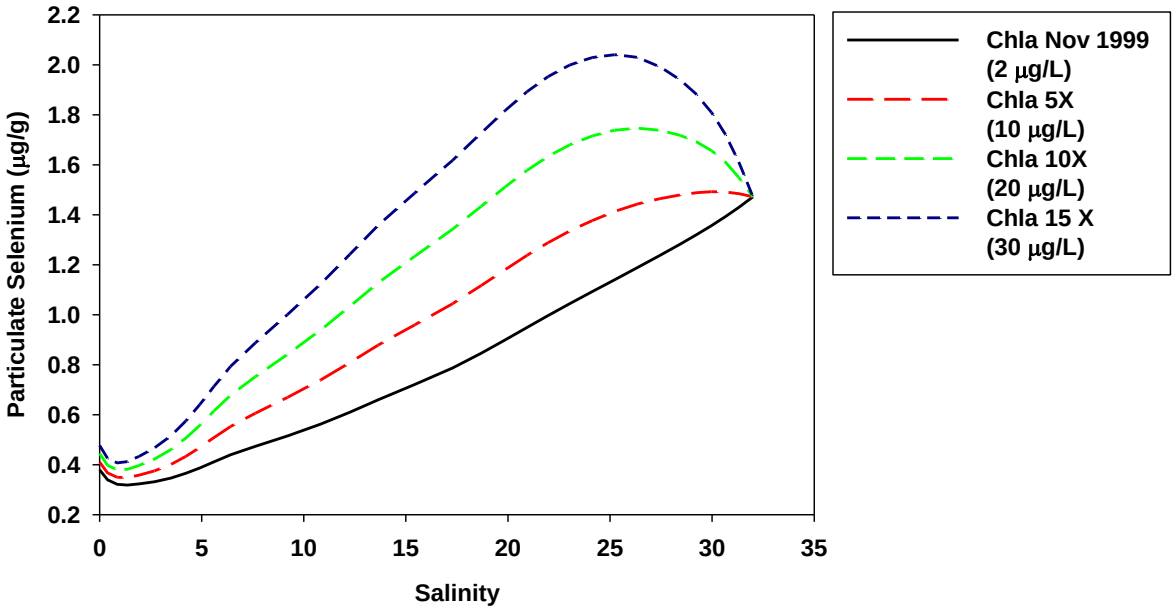


Figure 4-6 **Simulated particulate selenium concentration (in µg/g) in response to different chlorophyll a concentration levels.**

A test case using monthly estuary mean observed chlorophyll a concentrations in simulating phytoplankton uptake of selenium was run. The model was also run under the scenario of higher chlorophyll a concentration in seawater (4 µg/L). The results indicated differences in predicted particulate selenium concentrations, particularly under low flow, but generally showed good agreement among different chlorophyll a concentrations (Figure 4-7).

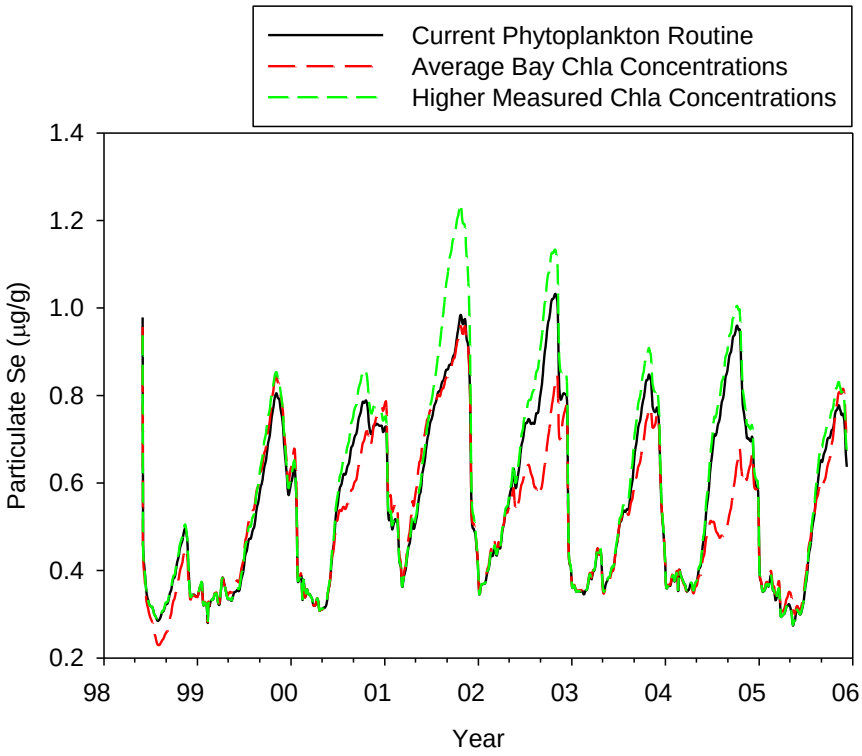


Figure 4-7 **Simulated particulate selenium concentration (in µg/g) in response to different methods for simulating phytoplankton.**

Overall, the tests varying chlorophyll a indicate the potential for significant impact to particulate concentrations. Indeed, highest chlorophyll a levels evaluated in Figure 4-6 have occurred in the Bay in the 1980s, and may do so again, depending on changing flows, temperature, and grazer abundance. However, in the range of concentrations now observed in the Bay and in the ocean, the differences due to chlorophyll a on particulate selenium are small, and the imperfections of the model calibration for chlorophyll a shown in Section 3 is unlikely to have had a major impact.

4.3. CALIBRATING UPTAKE AND MINERALIZATION BY PHYTOPLANKTON

The model parameterization presented in Section 3 used phytoplankton uptake and particulate organic selenide mineralization rate constants from the literature, following Meseck and Cutter (2006). These rate constants, were largely able to represent trends in dissolved and particulate selenium concentrations, as well as Se:C ratios in phytoplankton. The sensitivity of these rate constants was estimated by applying a ±50% change and discussed in Section 4.1. The model results for different selenium species were not found to be very sensitive over the range tested.

Given the importance of the uptake rates to the conversion of dissolved selenium to a form that can be readily assimilated by bivalves, and the paucity of literature values on uptake and mineralization rates of selenium, further exploration of these rate constants, going beyond the ±50% change, is helpful. If the model can be made to work with much higher uptake rates, it would imply a more rapid conversion of dissolved selenium to particulate selenium, and a more rapid response in particulate concentrations due to changing dissolved

concentrations. This is related to the ability to control bivalve uptake by controlling dissolved selenium concentrations in the bay.

The processes relating uptake of dissolved selenium species and the constituents constraining the calibration are shown in Figure 4-11. This is a subset of the all the selenium transformations considered in the model, and serves to explain the calibration of the uptake rate. In the testing that was performed, the uptake rate constants for selenite and dissolved organic selenide were raised by 10x and 100x their base calibration levels. In the base case calibration the selenate uptake rates were about 43% of the uptake rates for selenite. Selenate rates of uptake were not changed, because it is known that selenate uptake in a sulfate rich environment like NSFB is limited. As the model is currently set up, if the uptake rates are increased, there is an increase in the phytoplankton Se, and a decrease in the dissolved phase selenium concentrations. When the rate constants are increased by 10x and 100x, there is a depletion of the dissolved phase concentrations such that the observed data cannot be fit for Se(IV), Se(-II), and for the Se:C ratio in particulates. To fit the dissolved concentrations, and to prevent excessive buildup of Se in the phytoplankton compartment, the mineralization rate needs to be changed. The least squares best fits mineralization rates corresponding to the higher uptake rates are shown in Table 4-2. In effect, to fit the data, the mineralization rate needs to increases in the same proportion as the uptake rates; the 10x and 100x uptake rates correspond to similar increases in mineralization rate. A closer look at the dissolved phase data provides more insight into the processes. For the 10x case, the model fits for the dissolved phase are acceptable with a similar enhancement in mineralization rate. However, for the 100x case, even with the hundred-fold increase in mineralization rate, the fits for dissolved selenium are poor, and systematically different from the data. This exercise illustrates that the uptake rates are bounded to within a factor of 10 from the original calibration. Any increase in the uptake rates must be accompanied by an increase in the mineralization rate, such that the ratio of the uptake and mineralization is similar.

From the perspective of the TMDL, additional testing showed similar responses in bivalves to dissolved load changes for either the base case or the 10x uptake rate case, the latter associated with a 10x increase in mineralization rate. Thus, the base case uptake calibration is generally robust for application to the TMDL and for testing load changes in NSFB.

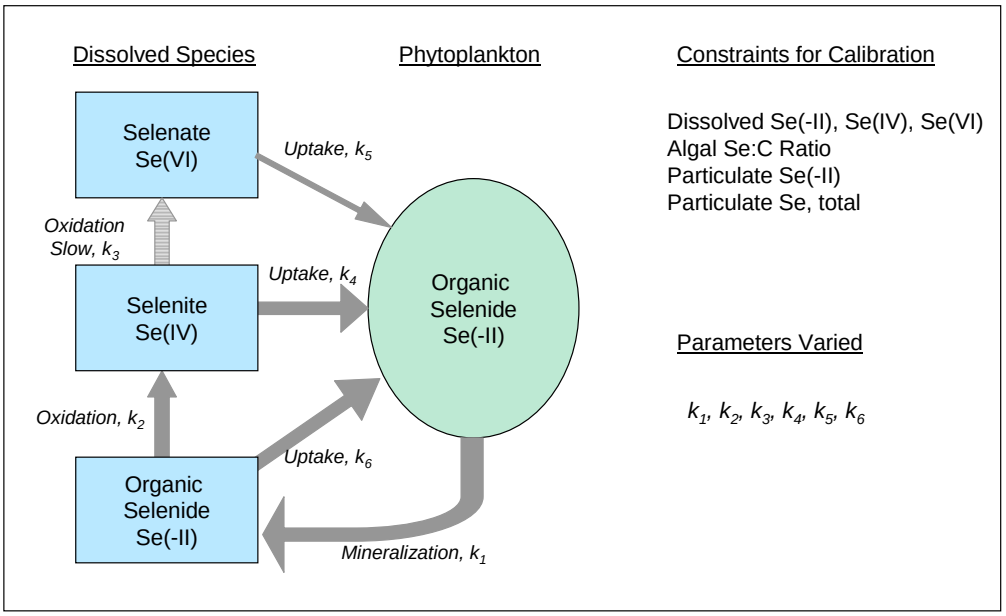


Figure 4-8 **Processes related to phytoplankton uptake of various dissolved species, and mineralization to convert particulate organic selenide to dissolved organic selenide. Also shown are the different constituents that constrain calibration, and the parameters that may be varied to fit observed data.**

Table 4-2
Changing Mineralization Rate as a Result of Changing Uptake Rates

	Uptake (l/ug Chla day)			Calibrated Mineralization Rate (1/day)
	k4 (SeIV)	k5 (SeVI)	k6 (Se-II)	k1 (POrgSe)
Base Case	0.000379	0.000081	0.000189	0.00657
10x	0.003787	0.000081	0.001894	0.0592
100x	0.037872	0.000081	0.018936	0.666

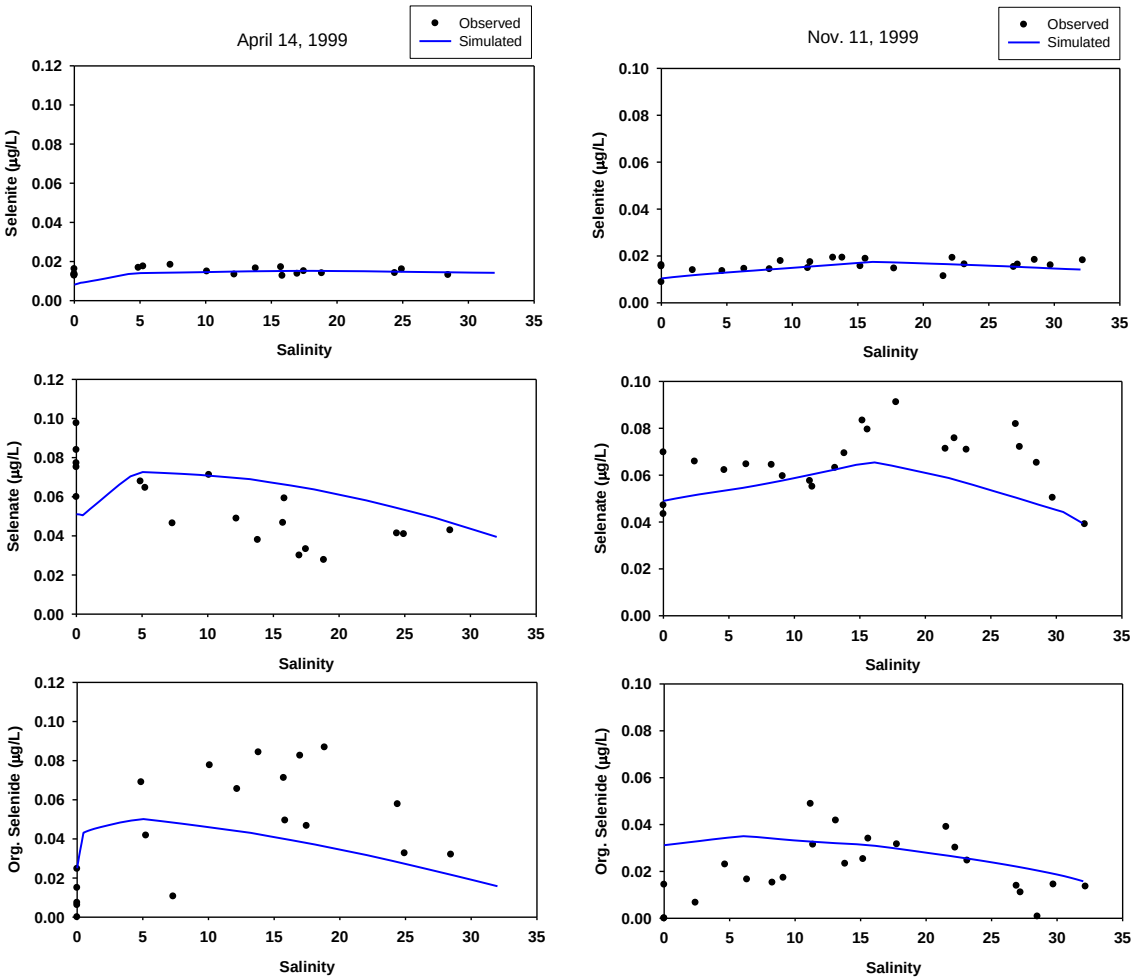


Figure 4-9 **Dissolved phase selenium concentrations when uptake rates for selenite (Se(IV)) and selenide (Se(-II)) are raised by a factor of 10 from their base case values. The best fit to data was by least squares minimization, and resulted in mineralization rates that were higher than base case rates by a factor of 10 as well.**

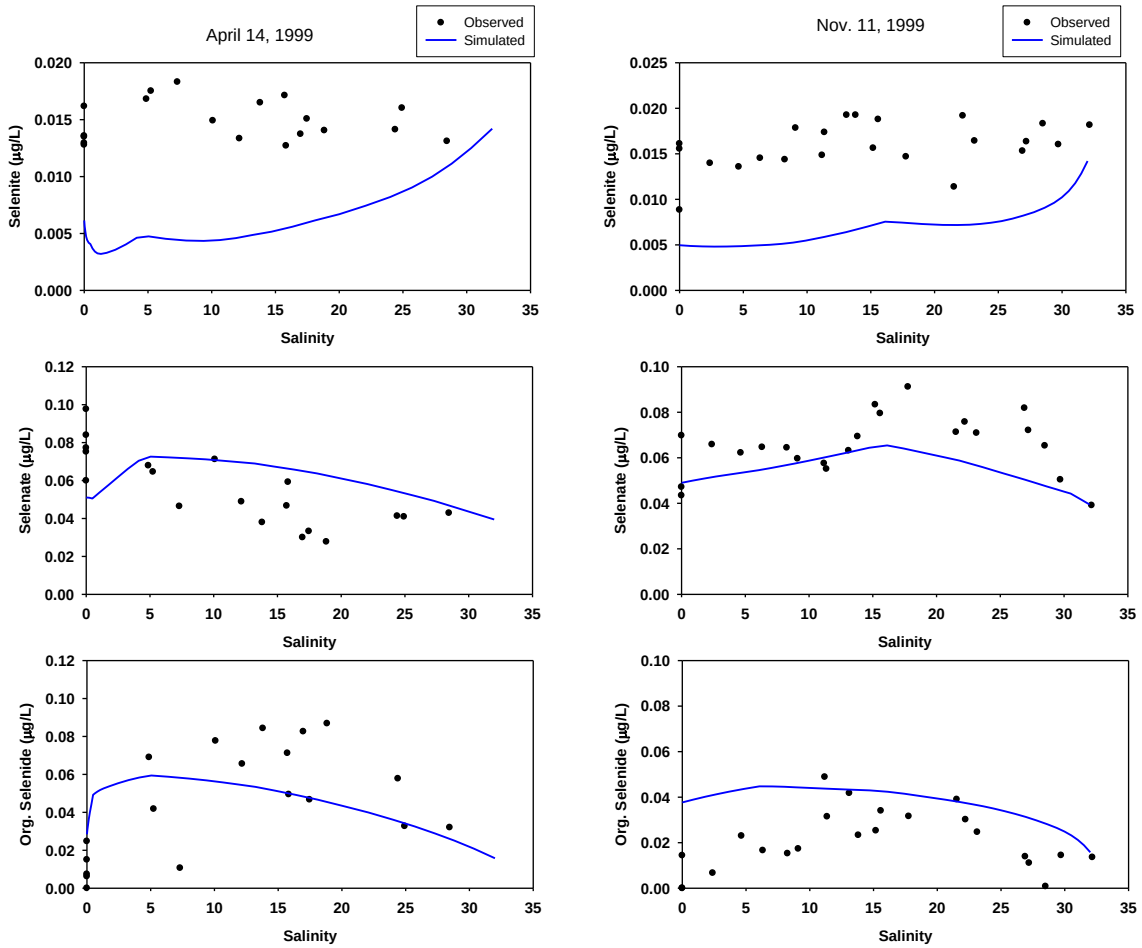


Figure 4-10 **Dissolved phase selenium concentrations when uptake rates for selenite (Se(IV)) and selenide (Se(-II)) are raised by a factor of 100 from their base case values. The best fit to data was by least squares minimization, and resulted in mineralization rates that were higher than base case rates by a factor of 100 as well. However, even with this change, the selenite was significantly depleted compared to the data, suggesting that this uptake rate is too high.**

4.4. VARYING SEAWATER AND RIVERINE BOUNDARY PARTICULATE SELENIUM CONCENTRATIONS

4.4.1 Lowering Seawater Endmember

Particulate selenium concentrations in the seawater endmember are not well defined. The approach used in Section 3 is to calibrate using field data. This resulted in a seawater boundary value of 1.22 µg/g, which may be compared with a reported value by Cutter and Bruland (1984) of 1.69 µg/g at a depth of 50m in the Pacific Ocean. An alternative is to use particulate selenium concentrations measured at Golden Gate by Doblin et al. (2006) as the seawater endmember concentrations for particulate selenium, (~0.9 µg/g). This boundary values results in simulated particulate selenium concentrations are lower, particularly near the mouth of the estuary (Figure 4-11).

Simulated selenium concentrations in bivalves over long-term periods show some difference from the original simulation. Simulated selenium concentrations in bivalves at Carquinez Strait are slightly lower than in the original simulation. The difference is more evident

during low flow, with the largest difference up to 1 µg/g (Figure 4-12). With the lower seawater end member concentration, simulated particulate selenium concentrations in µg/L still compared reasonably well to the observed data (Figure 4-13 and Figure 4-14).

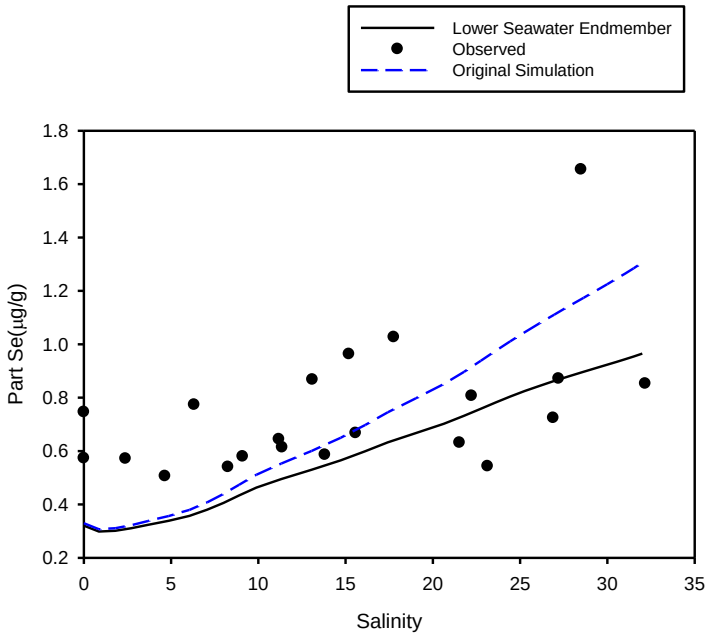


Figure 4-11 **Model simulated particulate selenium using lower seawater endmember for a low flow period (November 1999), compared to original simulation.**

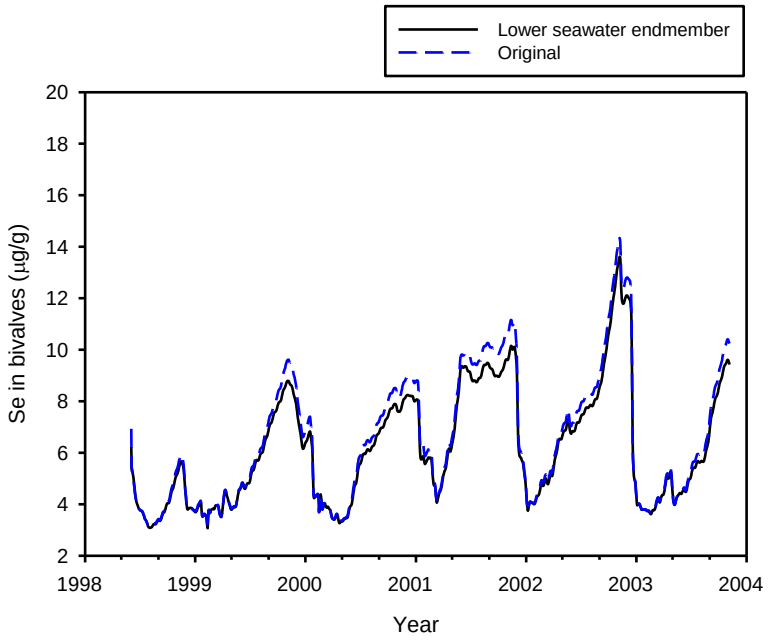


Figure 4-12 **Model simulated selenium concentrations in bivalves using lower seawater end member, compared to the original simulation.**

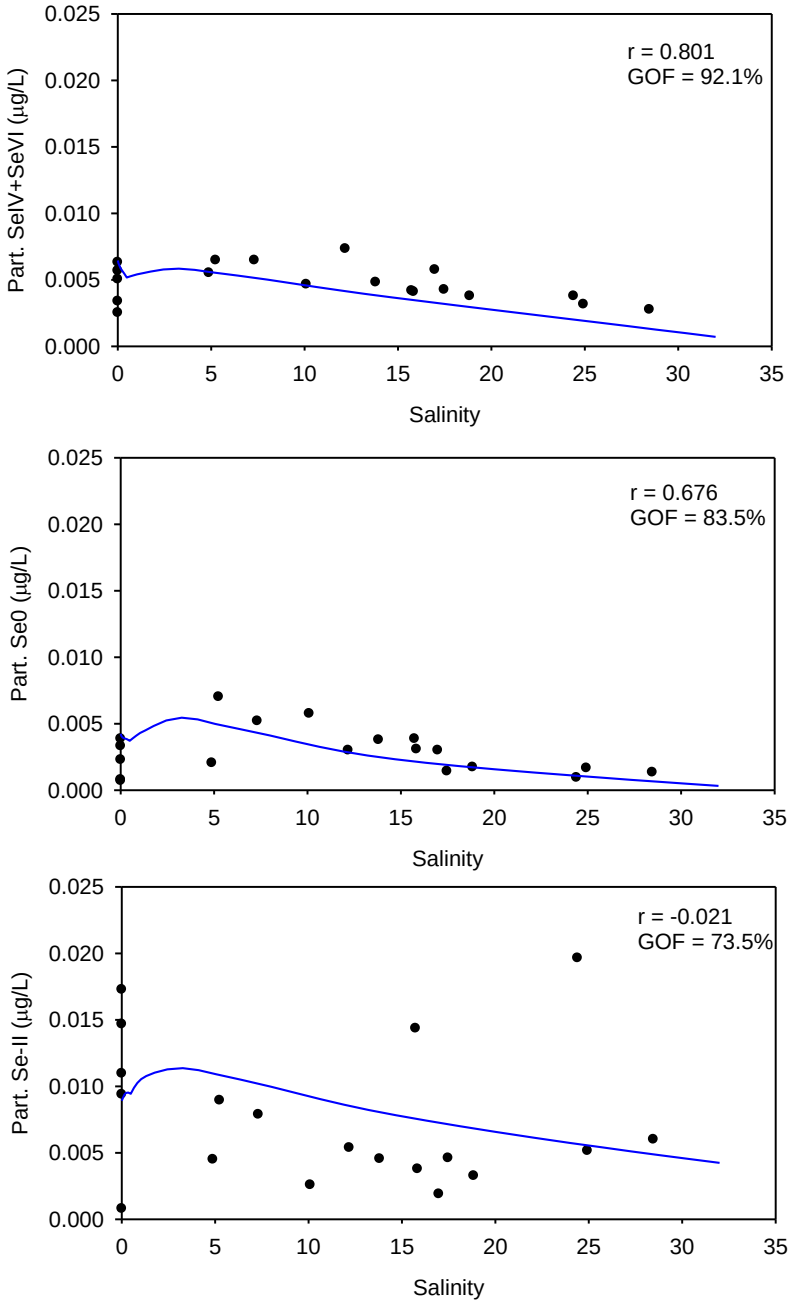


Figure 4-13 **Model simulated particulate selenium concentrations (in µg/L) using lower seawater endmember particulate selenium concentration for high flow period (April, 1999).**

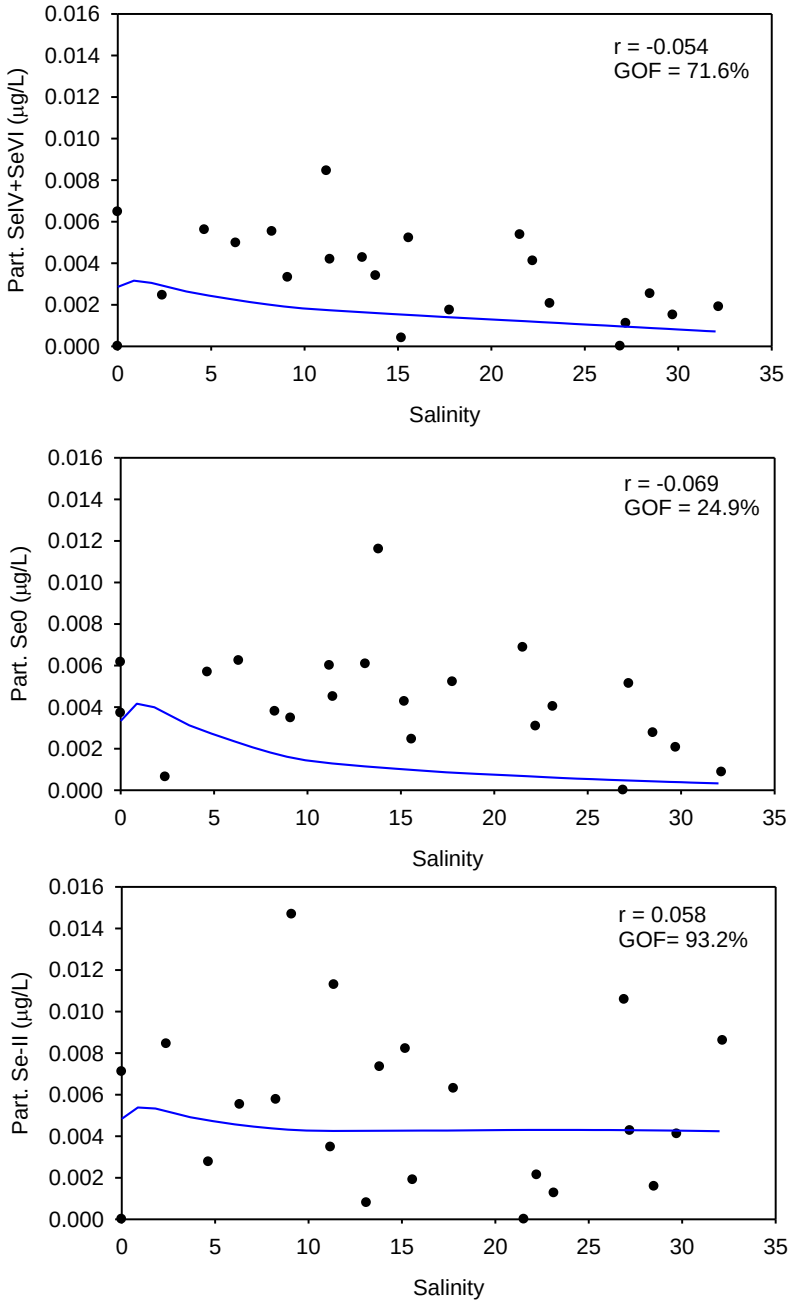


Figure 4-14 **Model simulated particulate selenium concentrations (in µg/L) using lower seawater endmember particulate selenium concentration for a low flow period (November, 1999).**

4.4.2 Impacts of Varying Riverine Endmember Concentrations

Particulate selenium concentrations at the riverine endmember measured by Doblin et al. (2006) ranged from 0.08-0.40 µg/g for particulate elemental selenium, 0.25 µg/g for particulate selenite and selenate and 0.015-0.74 µg/g for particulate organic selenide. Total particulate selenium concentrations also show some variation ranging from 0.357 to 0.747 µg/g at Rio Vista (n = 4; Doblin et al. 2006). For the calibration period of 1999, riverine

particulate selenium concentrations for different species were determined through calibration. The calibration objective was to derive the riverine particulate selenium concentrations that result in best fit of particulate selenium species (in μg/L) with the observed data. To evaluate the effects of varying riverine particulate selenium concentrations in model predictions, high and low riverine endmember selenium concentration scenarios were formulated. The high and low riverine particulate selenium scenarios were formed through specifying upper bound and lower bound of particulate selenium concentrations associated with PSP, BEPS and phytoplankton, respectively.

To test the impact of varying riverine particulate selenium concentrations associated with PSP, BEPS and phytoplankton, the higher and lower bounds of particulate selenium concentrations associated with PSP (mean ± standard deviation) based on observed data in Sacramento River at Rio Vista were used (for PSe0 and PSeivvi). For particulate organic selenide, the minimum and maximum particulate organic selenide concentrations were used.

For Se:C uptake ratios measured in the Delta, Se:C uptake ratio for bacteria is higher at about 32 μg/g, and Se:C uptake ratios by phytoplankton are about 11 μg/g. These values were used in specifying higher and lower end of particulate selenium associated with phytoplankton. Selenium concentrations on particulates used in testing the effects of riverine boundary conditions are listed in Table 4-3.

Table 4-3
Upper and Low Bound of Particulate Selenium Concentrations Used in Riverine Endmembers

	PSP (PSeivvi)	PSP (PSe0)	PSP (POrgSe)	PSP (total Part. Se)	BEPS (total Part. Se)	Se:C ratio in riverine phytoplankton
Upper bound (μg/g)	0.257	0.407	0.740	1.404	0.269	31.80
Lower bound (μg/g)	0.041	0.132	0.015	0.188	0.054	11.13

The use of higher and lower bounds of riverine endmember particulate selenium concentrations result in simulated particulate selenium concentrations in the estuary (in μg/g) to be significantly different from the base case (Figure 4-15). Simulated selenium concentrations in bivalves over the long-term are also significantly different from the base case (Figure 4-16).

The changes in riverine end member concentrations of particulate selenium have some impacts on simulations of particulate selenium concentrations (in μg/L) during high flow, with predicted particulate selenium greater than observed using the higher boundary condition. Simulated particulate selenium concentrations (in μg/L) during low flow compared reasonably to both low and high riverine boundary conditions (Figure 4-17), a reflection of the substantial variability in the particulate selenium data in the bay. The model predictions of particulate selenium (μg/l) for high flow conditions, do not compare well to the data for the higher riverine boundary condition.

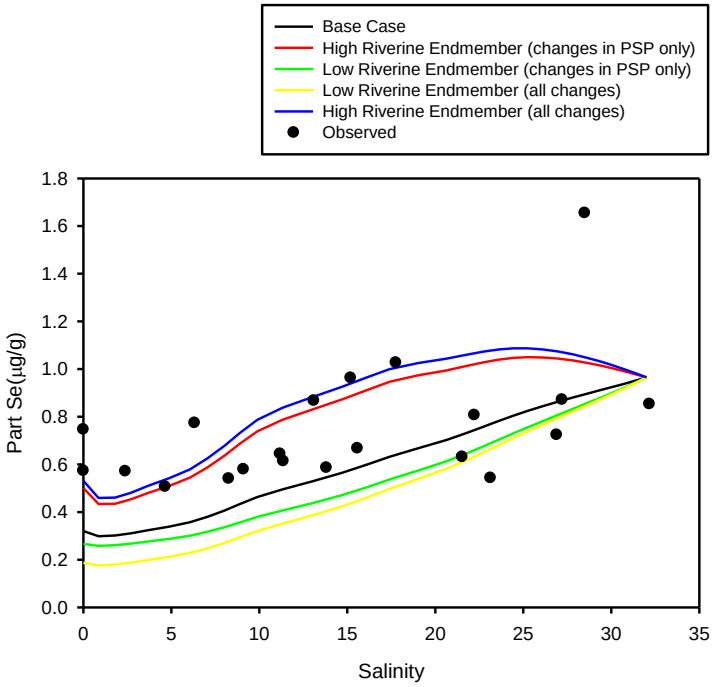


Figure 4-15 **Simulated particulate selenium concentrations (in µg/g) using higher and lower particulate selenium concentrations in the riverine end member.**

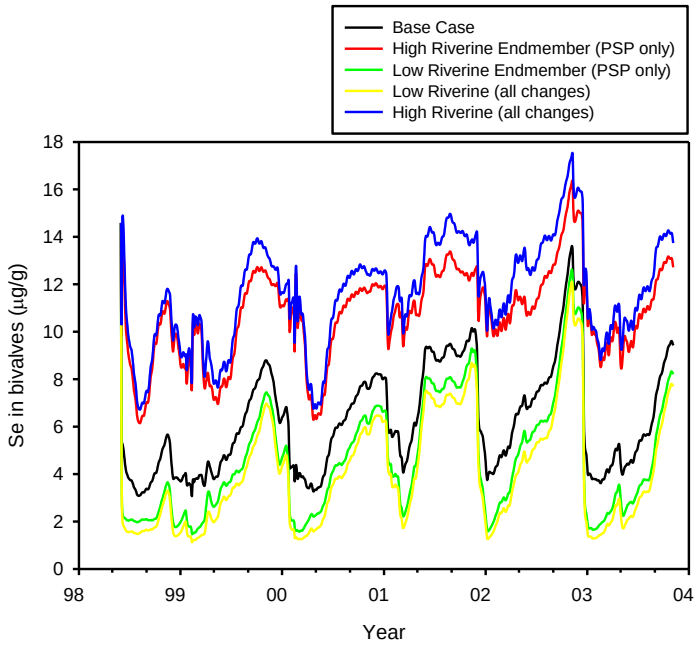


Figure 4-16 **Simulated selenium concentrations in bivalves using higher and lower riverine end member concentrations of particulate selenium.**

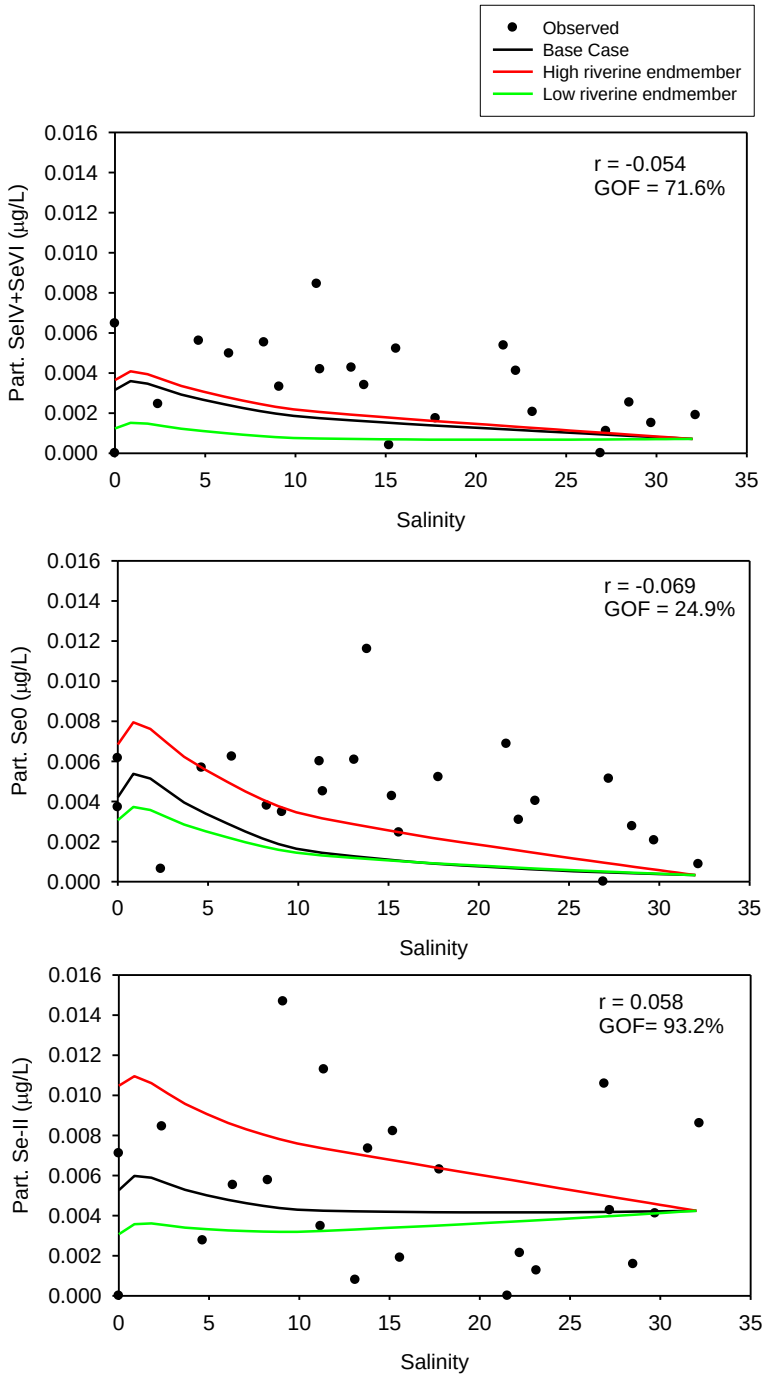


Figure 4-17 **Model simulated particulate selenium concentrations (in µg/L) under a low flow period (November, 1999) using higher and lower riverine end member concentration of particulate selenium.**

4.4.3 Higher and Lower Bounds of Riverine and Seawater Endmember Concentrations

Based on the preceding presentation of varying seawater and riverine boundary values, and the limited data available to define each boundary, a lower and higher boundary of riverine particulate selenium concentrations can be used to add more robustness to the model predictions (Table 4-4). The use of a higher riverine boundary condition resulted in

significant over-predictions in particulate selenium (µg/l) during high flow, the higher boundary condition was only applied for the lower flow conditions (defined as NDOI < 1.5 x 10^{10} l/d). Two different particulate selenium concentrations in the seawater endmember could also be used. The resulting estuarine particulate selenium during a low flow period (November 11, 1999) using the lower and higher boundary riverine and sweater endmember concentrations are able to better capture the range in the observed data (Figure 4-18).

The model predicted selenium concentrations in bivalves using the lower and higher riverine and seawater boundary conditions are shown in Figure 4-19. The range of boundary conditions will be used when the model is run in a predictive mode

Table 4-4
Lower and Higher Boundary of Rriverine and Sseawater Endmember Concentrations

	Riverine Boundary			Seawater Boundary	
	PSP PSe (µg/g)	BEPS PSe (µg/g)	Se:C in phytoplankton (µg/g)	PSP PSe (µg/g)	Se:C in phytoplankton (µg/g)
Lower Boundary	0.46	0.25	15.9	0.96	21.0
Higher Boundary (Applied when NDOI < 1.5 x 10^{10} l/d)	0.75	0.50	15.9	1.22	21.0

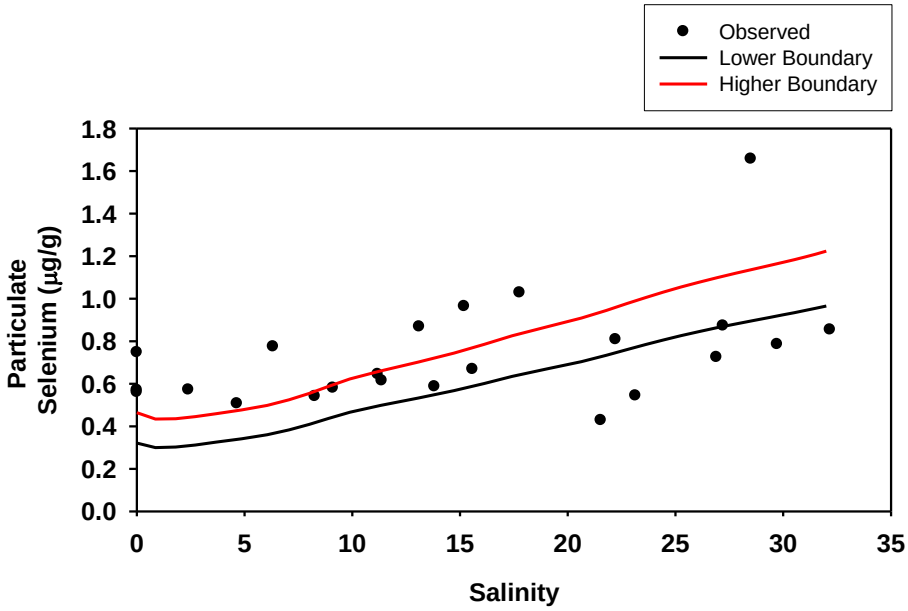


Figure 4-18 **Model simulated particulate selenium concentrations under upper and lower bounds of riverine and seawater endmember concentrations.**

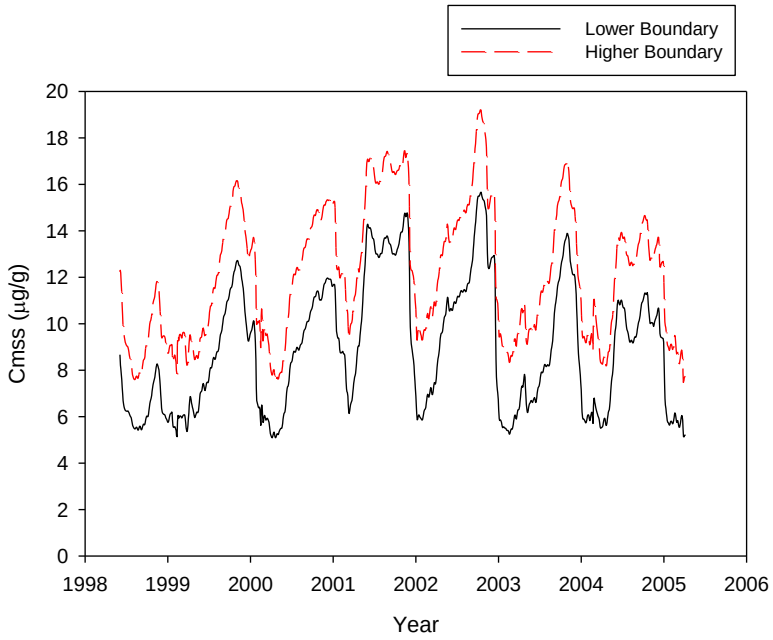


Figure 4-19 **Model simulated particulate selenium concentrations under upper and lower bounds of riverine and seawater endmember concentrations.**

4.5. RELATIVE CONTRIBUTION OF DIFFERENT SOURCES OF PARTICULATE SELENIUM

Particulate selenium is the primary uptake route of selenium by the bivalves. Different species of particulate selenium have different assimilation efficiencies. Particulate selenium can originate from the bed sediment (BEPS), the riverine input (PSP) and *in situ* transformation (phytoplankton uptake) and species composition may be different for these sources. A better understanding of the contribution of particulate selenium from these sources can help determine the effectiveness of management actions to be taken (whether emphasis can be placed on riverine particulate selenium or selenium from bed sediments or reducing phytoplankton uptake by reduced dissolved selenium input).

Particulate selenium concentrations here are expressed both in µg/L and µg/g. For a low flow period, over the estuary, model simulated permanently suspended particulate (PSP) associated selenium comprises the largest portion of particulate selenium (Figure 4-20). Phytoplankton associated selenium is approximately half of the PSP associated selenium. Particulate selenium contribution from BEPS decreases from the head of the estuary, a pattern similar to TSM. For a specific location (Carquinez Strait), simulated time series of particulate selenium concentrations again indicated PSP selenium accounts for the largest portion of particulate selenium (Figure 4-21). All sources of particulate selenium appear to increase during high flow. During low flow, simulated phytoplankton associated selenium could be more significant than BEPS associated selenium. Overall, the composition of simulated estuary mean particulate selenium for November 11, 1999 is nearly 50% of permanent suspended particulates (PSP), with phytoplankton associated particulate selenium and particulate selenium associated with bed exchange materials accounting for 25% each (Figure 4-22).

In terms of loading, riverine inputs (TSM), are the largest source of particulate selenium loads to the estuary, followed by phytoplankton uptake (Figure 4-23). Due to the relatively balanced sediment erosion and deposition, net particulate selenium loadings from the estuary are small.

A few cases were run to test the effects of each individual source of particulate selenium on predicted particulate selenium (in μg/g). These are a case with removal of all riverine inputs of particulate selenium, a case assuming no selenium uptake by phytoplankton and no riverine phytoplankton input, and a case with no sediment-water exchange. The results are shown in Figure 4-24 and Figure 4-25. For a low flow period (November 11, 1999), removing bed exchange processes results in a small change in predicted particulate selenium. Assuming no phytoplankton uptake of selenium results in a decrease in particulate selenium along the estuary, due to mineralization of particulate organic selenium to dissolved organic selenide and dilution (or mixing) by seawater. Assuming no riverine inputs of particulate selenium, particulate selenium concentration at low to mid-salinities is about one-third of the original concentrations, although the differences become smaller with proximity to the seawater boundary.

Predicted particulate selenium concentrations (Figure 4-24 and Figure 4-26) indicated that net bed exchange contributes a small portion of the particulate selenium along the estuary. Uptake by phytoplankton accounts for a larger portion of the particulate selenium. Phytoplankton uptake plays an important role in maintaining high particulate selenium concentrations in the San Pablo Bay and Central Bay. Particulate selenium inputs from the rivers contribute to the largest portion of the particulate selenium. Riverine inputs of the particulate selenium are mostly comprised of more bio-available particulate organic selenide and particulate selenite + selenate. Phytoplankton uptake results in particulate organic selenide that is readily assimilated by clams. As for the TMDL, reductions in riverine inputs of particulate selenium or phytoplankton-associated selenium are likely to have a greater effect in achieving lower selenium concentrations in bivalves.

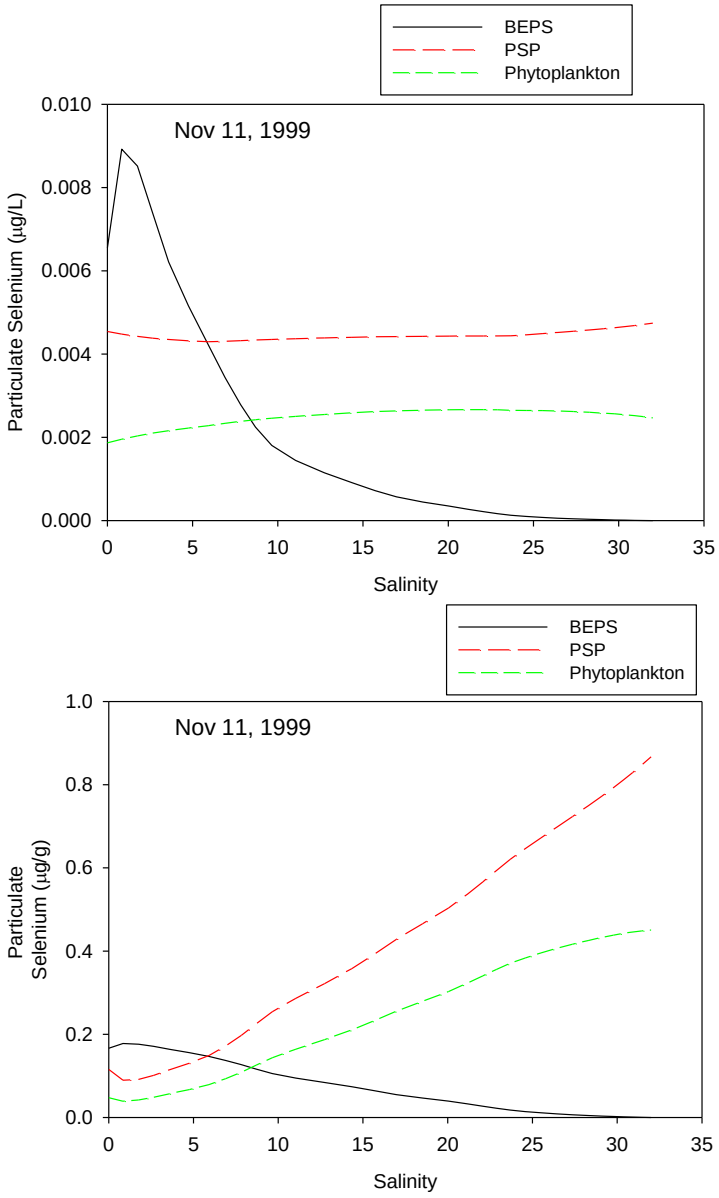


Figure 4-20 **Particulate selenium along the salinity gradient as contributions from permanently suspended particulates (PSP), bed exchange particulates (BEPS) and phytoplankton for a low flow period (November 11, 1999). Riverine particulate selenium: 0.467 µg/g, Seawater particulate selenium: 1.22 µg/g.**

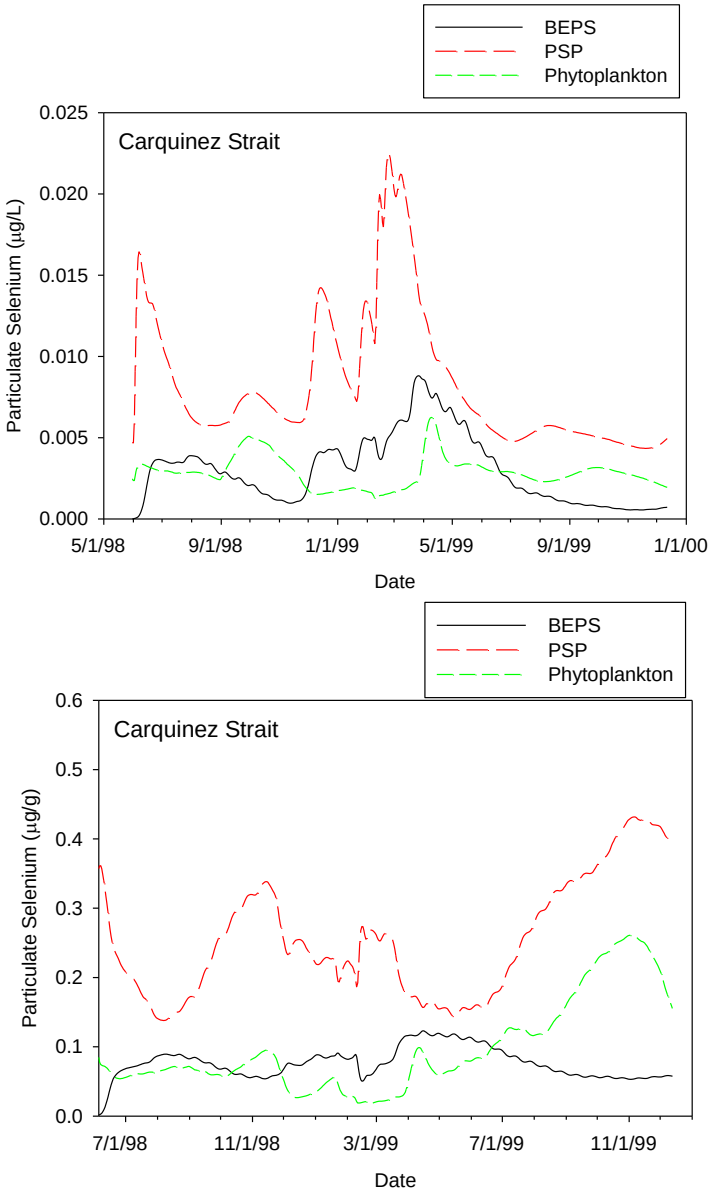


Figure 4-21 **Particulate selenium at Carquinez Strait (X = 47,439 m from Rio Vista) over time as contributions from permanently suspended particulates (PSP), bed exchange particulates (BEPS) and phytoplankton[4].**

[4] Particulate Se in phytoplankton is dominated by organic Se. Se in PSP and BEPS can be comprised of adsorbed selenite and selenate, elemental selenium and organic Se.

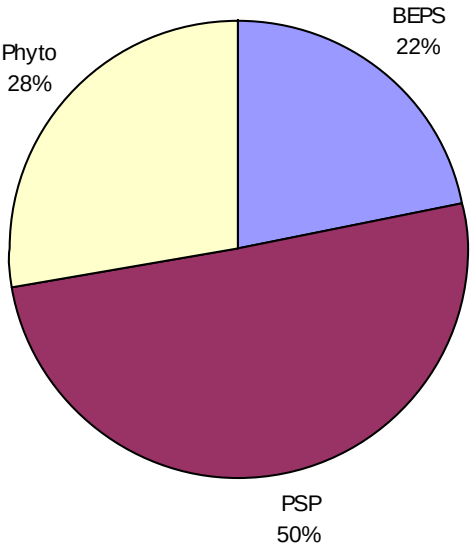


Figure 4-22 **Contribution of different sources to the mean particulate selenium concentrations in NSFB for November 11, 1999.**

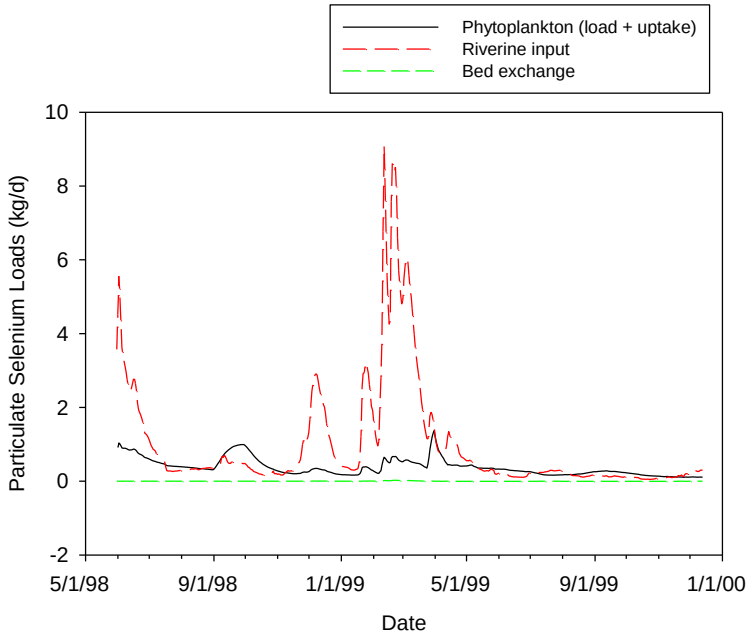


Figure 4-23 **Model predicted particulate selenium load inputs from riverine input, phytoplankton uptake and bed exchange.**

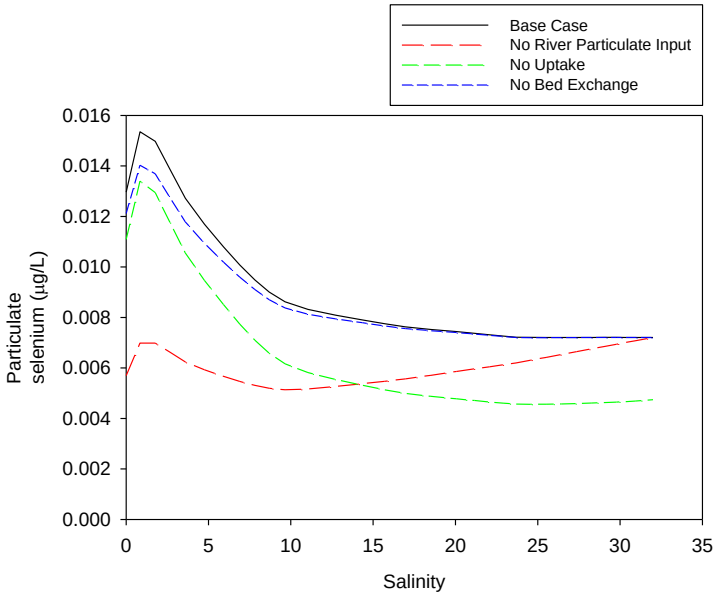


Figure 4-24 **Model predicted particulate selenium concentrations (in µg/L) under scenarios of no riverine particulate selenium input, no phytoplankton uptake, and no bed exchange.**

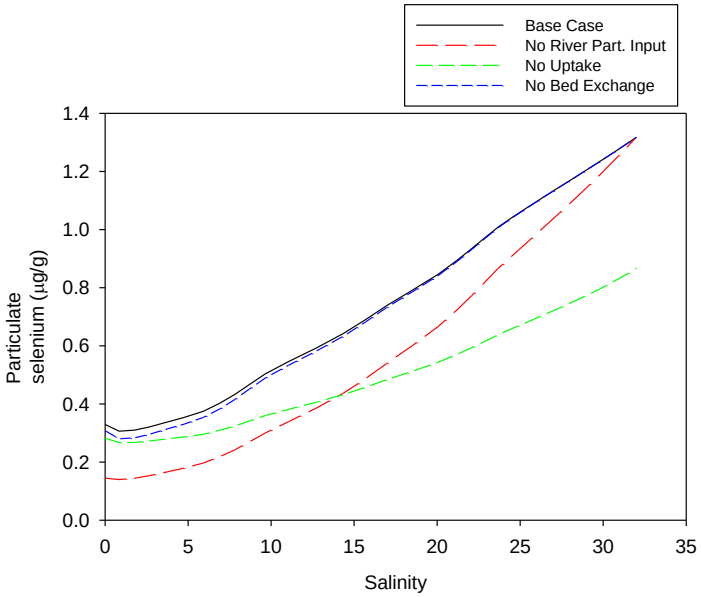


Figure 4-25 **Model predicted particulate selenium concentration (in µg/g) under scenarios of no riverine particulate selenium input, no phytoplankton uptake and no bed exchange.**

4.6. MASS BALANCE OF SELENIUM

Annual budgets of dissolved and particulate selenium suggested that outflow from the Bay is the largest loss mechanism (Figure 4-26 and Figure 4-27). For the water years simulated, outflow of dissolved and particulate selenium balances selenium input from all sources including riverine input and local point sources. For some years selenium was gained in storage in the water column, but was lost in the next year.

Bacteria, algae and plants can form dimethylselenide and dimethyldiselenide that can be volatilized to the atmosphere (Ansede and Yoch, 1997). Dimethylselenide loss to the atmosphere can be up to 30% in the wetland/marsh systems (Zhang and Moore, 1997; Hansen et al., 1998). Volatilization of selenium in open water ecosystems (e.g., in bays) is less well known. For the purpose of this analysis, volatilization was not considered to be a significant loss mechanism.

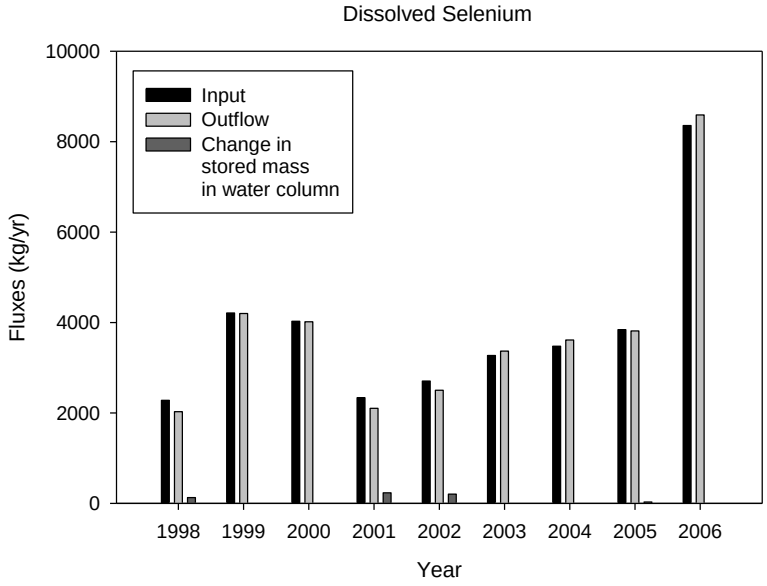


Figure 4-26 Model simulated mass balance of dissolved selenium for the period of 1998-2006

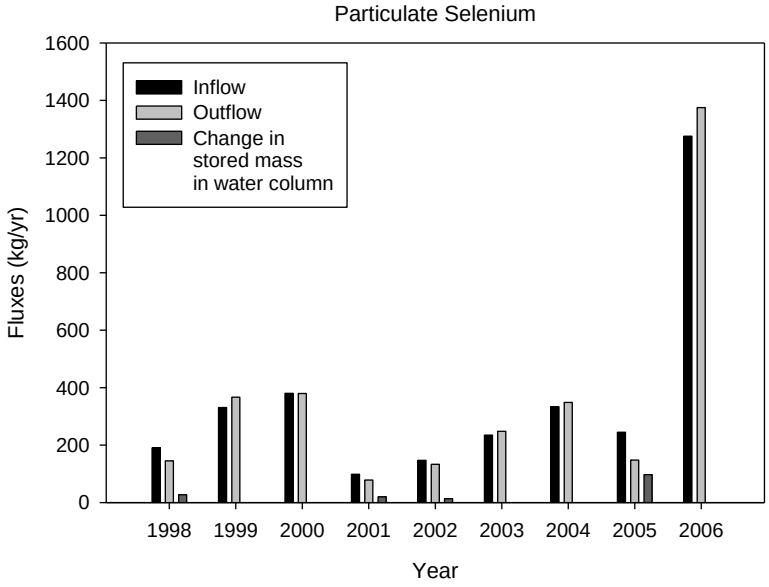


Figure 4-27 Model simulated mass balance of particulate selenium for the period of 1998-2006

A more detailed conceptual diagram of sources and sinks of dissolved and particulate selenium are shown for water years 1999, 2005, and 2006 for the NSFB (Figure 4-28 to Figure 4-33). Dissolved selenium loads from the San Joaquin River are approximately equal

to the Sacramento River input. Local tributaries represent the second largest inputs of dissolved selenium following the riverine inputs, followed by refinery loads and POTWs. Tributary and refinery loads show some variation among the years. The South Bay represents a larger input of dissolved selenium than POTWs. The overall load inputs of dissolved selenium are approximately equal to outflow to ocean water.

For particulate selenium, riverine inputs from Sacramento River at Rio Vista vary by a factor of 1.5 depending on the riverine boundary condition used. Overall particulate selenium inputs from the Sacramento River at Rio Vista were much higher than inputs from the San Joaquin River at the confluence (by a factor of approximately 7). Outflow of particulate selenium to the ocean was approximately equal to loads of particulate selenium. In current version of the model, particulate selenium loads from the refineries and the tributaries were assumed to be zero. The model predicted net outflow of particulate selenium from bed sediment (loss of particulate selenium associated with BEPS) ranged from 17.7 kg/yr in 2005 to 115.2 kg/yr in 2006, and were lower than the previous estimate of loss of 285 kg/yr due to net sediment erosion in TM2. This is likely due to the fact that the model is currently under-predicting the active bed sediment mass.

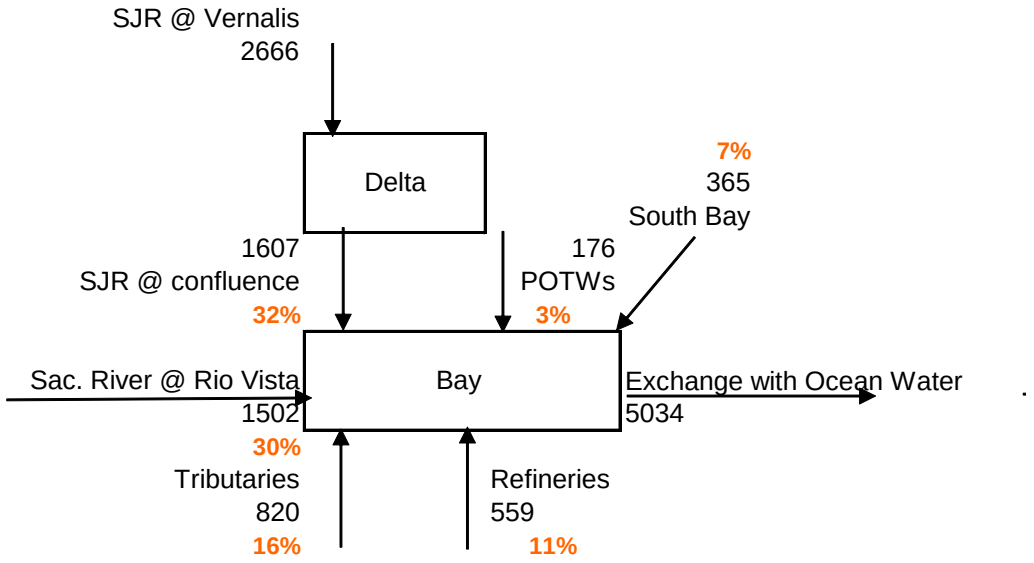


Figure 4-28 Sources and sinks of dissolved selenium in the NSFB for water year 1999 (kg/yr). Percentages of each source contributing to total load are also shown.

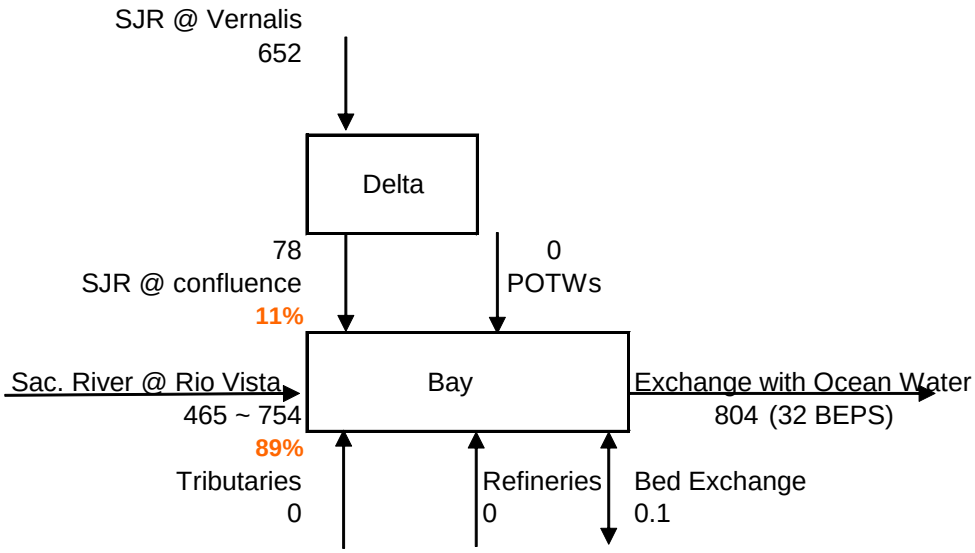


Figure 4-29 **Sources and sinks of particulate selenium in the NSFB for water year 1999 (kg/yr). Loads are also shown as a percentage of combined Sacramento and San Joaquin River load.**

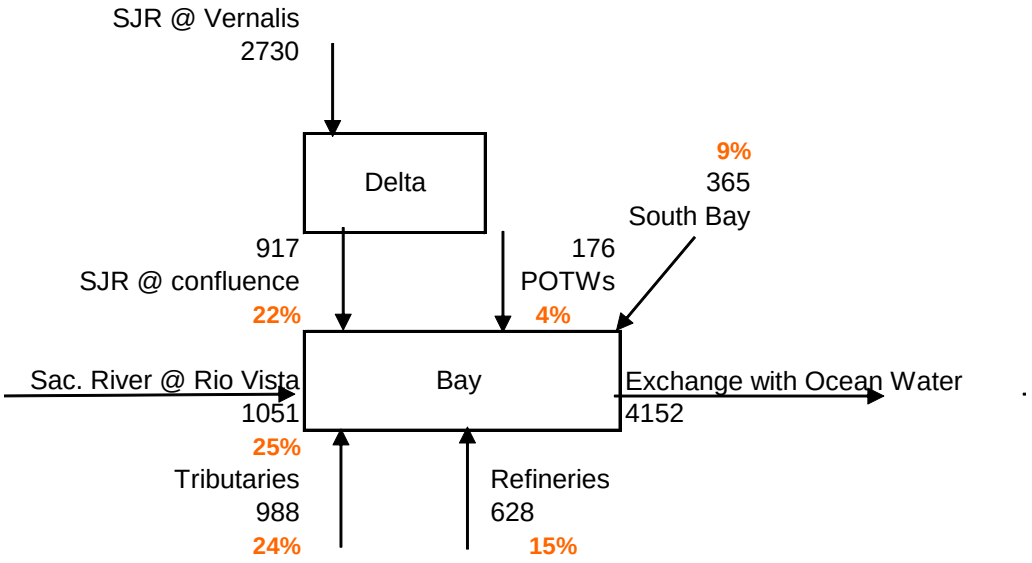


Figure 4-30 **Sources and sinks of dissolved selenium in the NSFB for water year 2005 (kg/yr). Percentages of each source contributing to total load are also shown.**

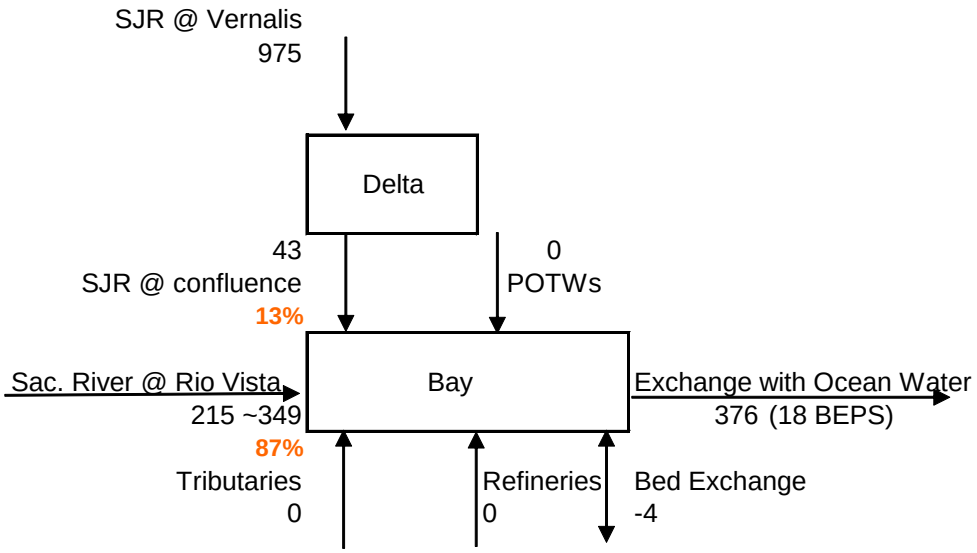


Figure 4-31 **Sources and sinks of particulate selenium in the NSFB for water year 2005 (kg/yr). Loads are also shown as a percentage of combined Sacramento and San Joaquin River load.**

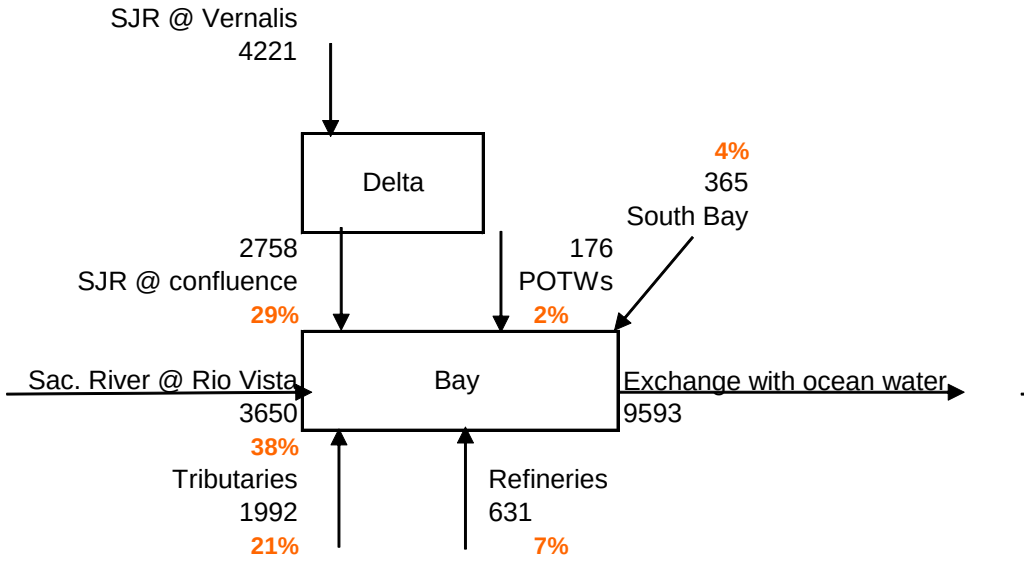


Figure 4-32 **Sources and sinks of dissolved selenium in the NSFB for water year 2006 (kg/yr). Percentages of each source contributing to total load are also shown.**

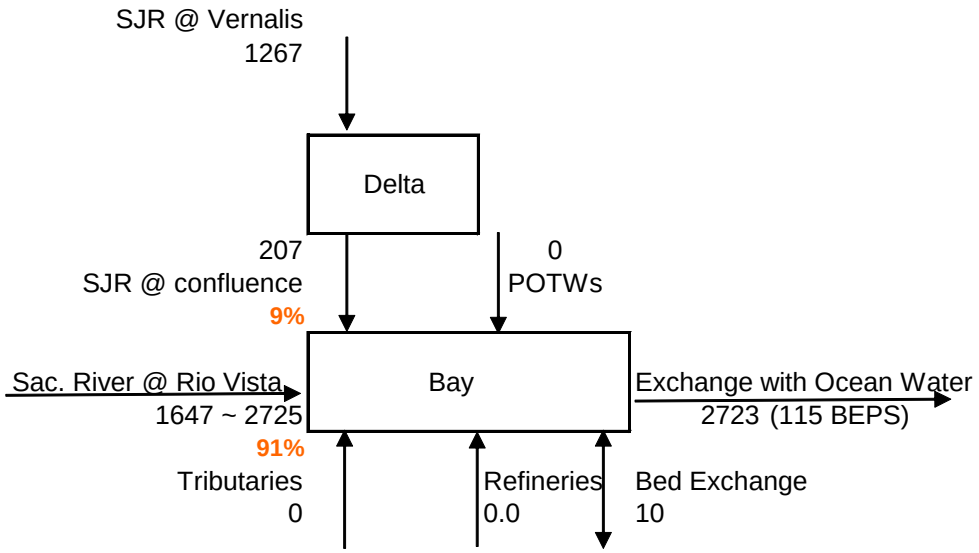


Figure 4-33 **Sources and sinks of particulate selenium in the NSFB for water year 2006 (kg/yr). Loads are also shown as a percentage of combined Sacramento and San Joaquin River load.**

Standing stocks of different species of selenium in the Bay are relatively constant on an annual basis but show seasonal variability due to variation in riverine and tributary input (Figure 4-34 and Figure 4-35). Dissolved selenium standing stock is comprised mostly of selenate, followed by organic selenide and selenite. Particulate organic selenide contributes to the largest percentage of the standing stock in particulate selenium, followed by particulate selenite and selenate, and particulate elemental selenium.

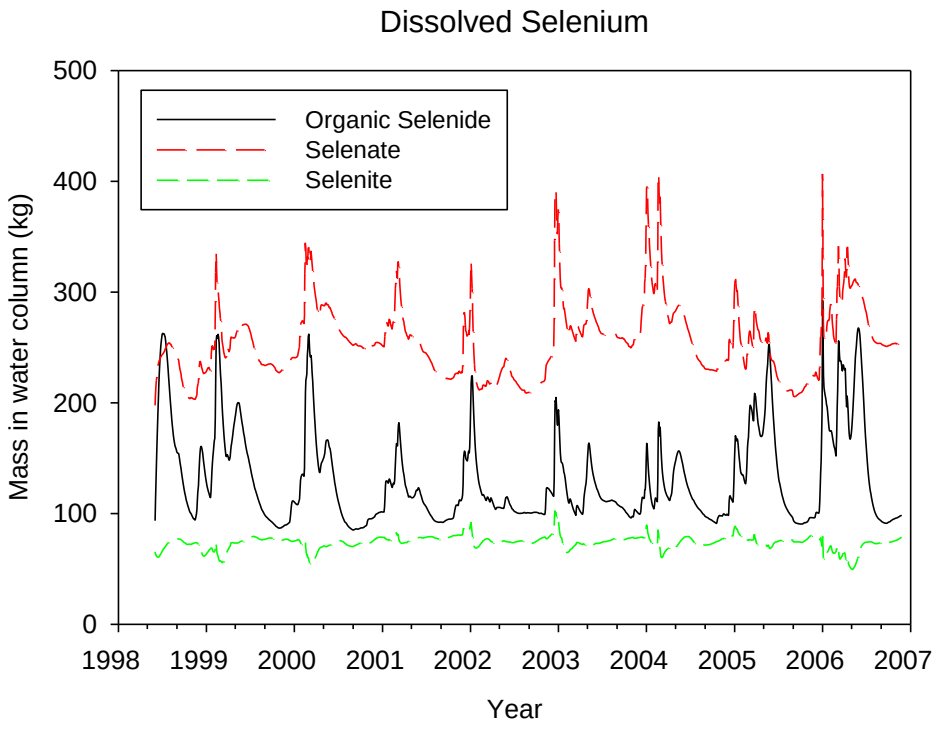


Figure 4-34 **Model simulated standing stock of dissolved selenium for the period of 1999-2006**

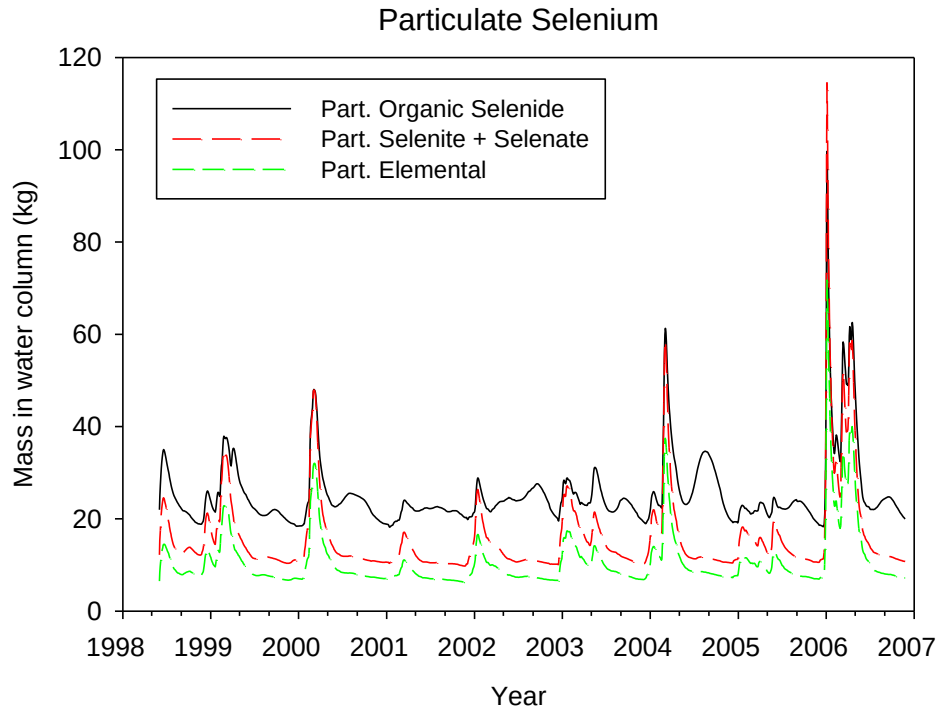


Figure 4-35 **Model simulated standing stock of particulate selenium for the period of 1999-2006**

Dissolved and particulate selenium undergo a series of transformations. Simulated transformations include phytoplankton uptake of selenite, selenate and organic selenide, mineralization of particulate organic selenide, and oxidation of dissolved organic selenide to selenite and selenite to selenate. The model simulated time series selenium transformation fluxes are shown in Figure 4-36. The oxidation of organic selenide to selenite is a relatively fast process and is the largest transformation flux simulated (0.4–1.1 kg/day). Mineralization of particulate organic selenide (BEPS, PSP, and phytoplankton associated) and the uptake of different species of dissolved selenium by phytoplankton are the second largest fluxes simulated (0.1-0.4 kg/day). Simulated selenium uptake fluxes by phytoplankton are higher during low flow. Adsorption and desorption is at a less significant level. Selenite oxidation is a much slower process and therefore simulated flux of selenite oxidation is at a much lower process.

Model simulated transformation fluxes on an annual basis for the simulation period of 1999-2006 are also shown in the bar diagram (Figure 4-37). Simulated mineralization of particulate selenium for the whole estuary is at rate of approximately 50 kg/yr. Selenium uptake by phytoplankton is at a rate of 50-120 kg/yr. Uptake of selenium by phytoplankton is about the same order of magnitude, although slightly higher than, mineralization of particulate organic selenium. Oxidation of organic selenide, Se(-II), to selenite, Se(IV) is at 150-250 kg/yr. Selenite oxidation to selenate, Se(VI), is negligible.

The mass balance plots presented in this section provide an error check, in that there is no loss or creation of mass, an essential test for a numerical model. The summary information on individual processes can be used to determine their relative significance, and better target future data collection as discussed in a subsequent section.

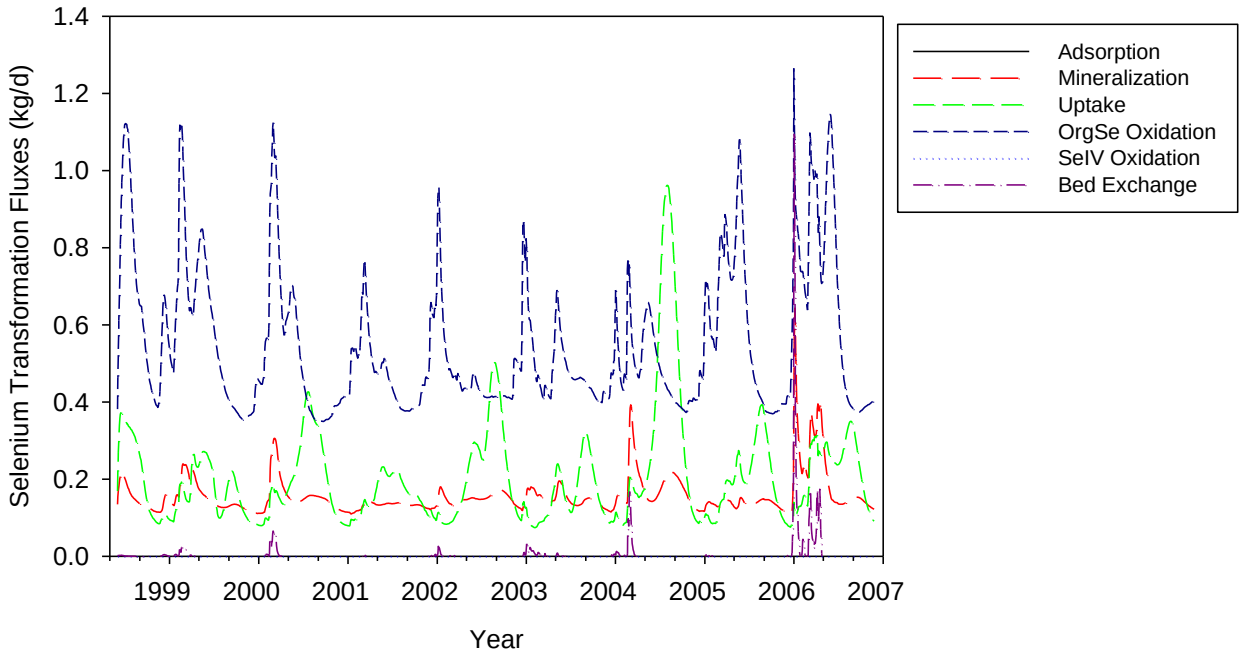


Figure 4-36 Model simulated selenium transformation for the period of 1999-2006

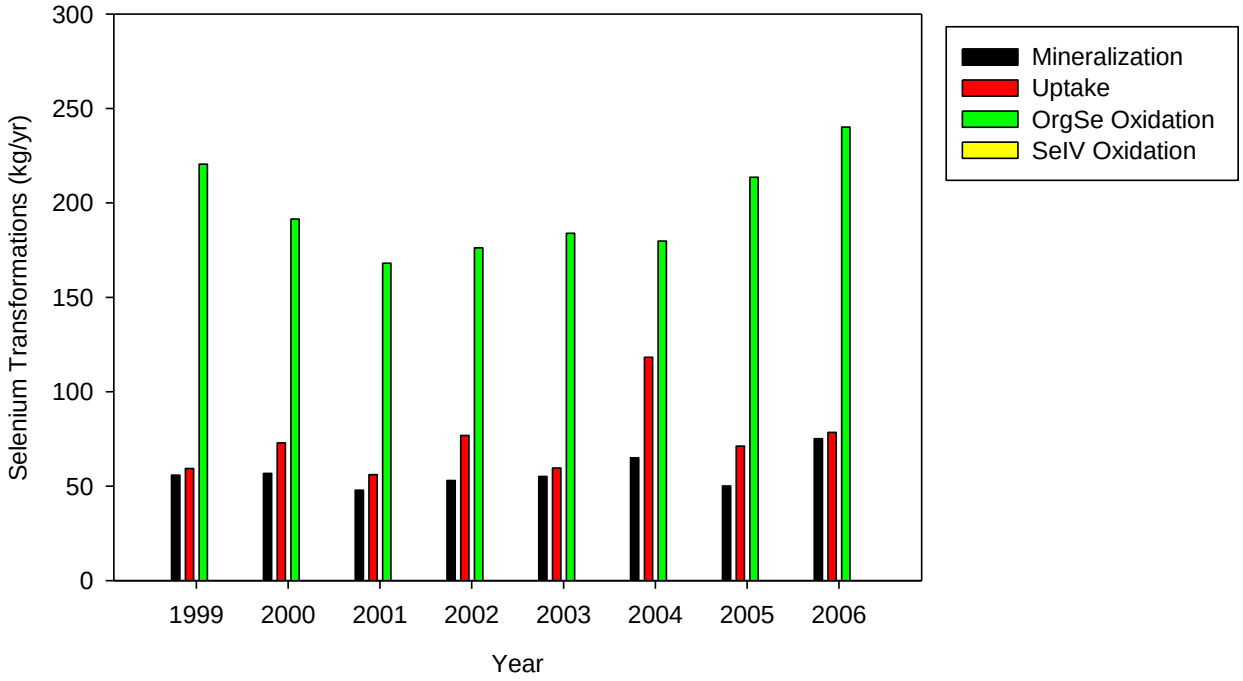


Figure 4-37 Model simulated selenium transformations for the period of 1999-2006

4.7. IMPACTS OF DOMINANT PHYTOPLANKTON SPECIES

Due to the variation of phytoplankton species through time and location in the estuary and large variations in selenium content associated with different phytoplankton species (Lehman, 2001; Baines et al. 2004), particulate selenium concentrations in the estuary may show large variation due to changes in phytoplankton species. Selenium concentrations in phytoplankton generally follow the order of golden brown algae > dinoflagellates> diatoms > green algae. Model simulations were conducted by assuming one dominant species of phytoplankton for each scenario to evaluate the impacts of phytoplankton species on particulate selenium.

The four scenarios include dominant species by golden brown algae (Se:C: 30.62 µg/g), diatom (*Chaetoceros gracilis*; Se:C 2.34 µg/g), green algae (0.248 µg/g) and diatom (*Skeletonema costatum*; 0.004 µg/g), with reported selenium content varying by several orders of magnitude among species. The predicted Se:C ratios are shown in Figure 4-38.

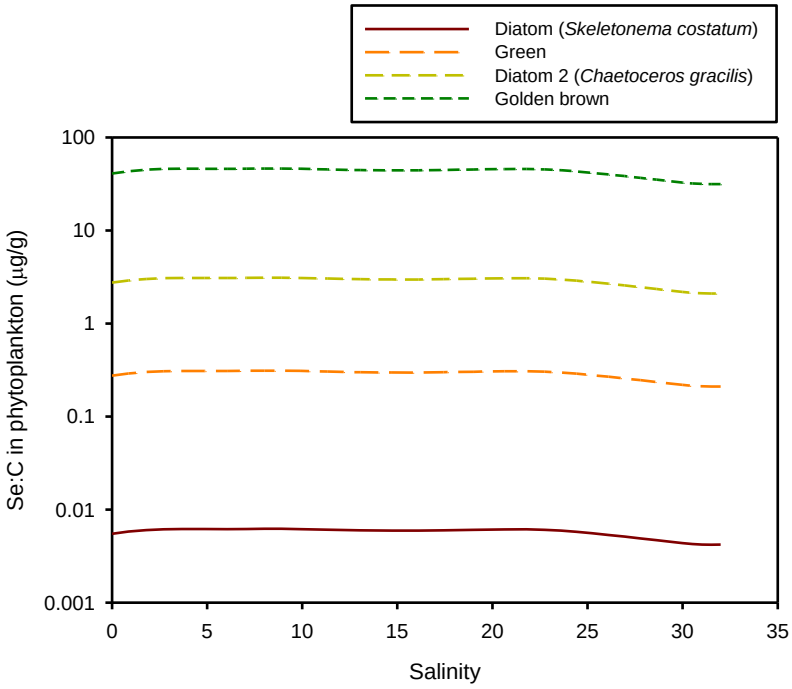


Figure 4-38 **Simulated Se:C in phytoplankton by assuming different dominant phytoplankton species in the estuary**

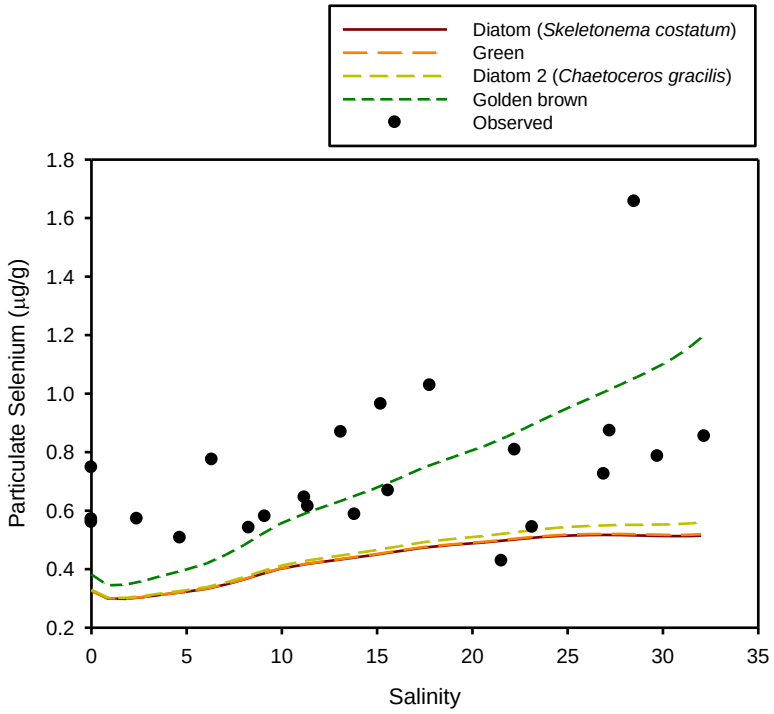


Figure 4-39 **Simulated particulate selenium concentrations (in µg/g) by assuming different dominant phytoplankton species in the estuary**

Simulated particulate selenium concentrations for golden brown algae are higher than other species and are more comparable with observed particulate selenium concentrations (Figure

4-39). Simulated selenium concentrations in bivalves also show a factor of 2-3 difference by different phytoplankton species. Particularly the golden brown algae resulted in significantly higher selenium concentrations in bivalves (Figure 4-40). In summary, if phytoplankton species shift from golden brown to green algae, lower selenium concentrations in particulates and bivalves and slower response in particulate selenium to load changes are expected.

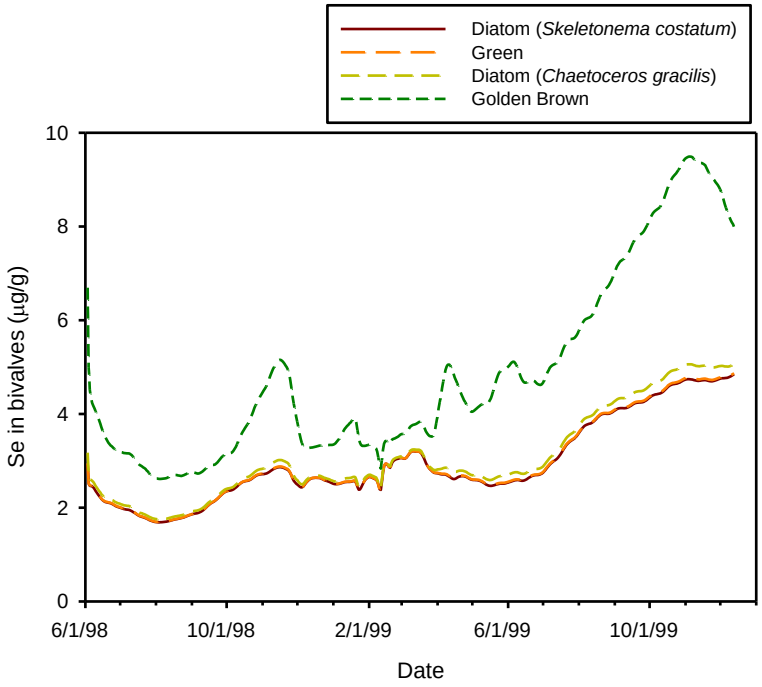


Figure 4-40 Simulated selenium concentrations in bivalves by assuming different dominant phytoplankton species.

4.8. COMPARISON WITH SPATIAL TRENDS IN PARTICULATE SELENIUM OBSERVATIONS

Particulate selenium in the estuary during low flows shows a small increasing trend with salinity. The increase appears to correspond with increases in chlorophyll a and pheophytin concentrations (Figure 4-41). The levels of chlorophyll a and phaeophytin seem to decrease slightly at salinity 20 and then e increase towards seaward boundary. The fraction of phytoplankton (in terms of biomass) in TSM increases with salinity (Figure 4-41, lower panel). Because phytoplankton concentrates selenium to a higher level than mineral particles, the increases in phytoplankton fraction in TSM can contribute to the elevated particulate selenium concentrations near the mouth of the estuary. As a result, particulate selenium concentrations show a positive correlation with fraction of phytoplankton in TSM (Figure 4-42). Even with selenium content in phytoplankton remaining constant through the estuary, the increases in phytoplankton fraction in TSM is able to explain a large portion of the increase in particulate selenium along the estuary.

For chlorophyll a, the high concentrations at the seawater end member are most likely due to both in situ production and advection from seawater. However it is difficult to differentiate from the measurements which process dominates. In the model, a seawater endmember concentration of 2.3 µg/L is specified for chlorophyll a.

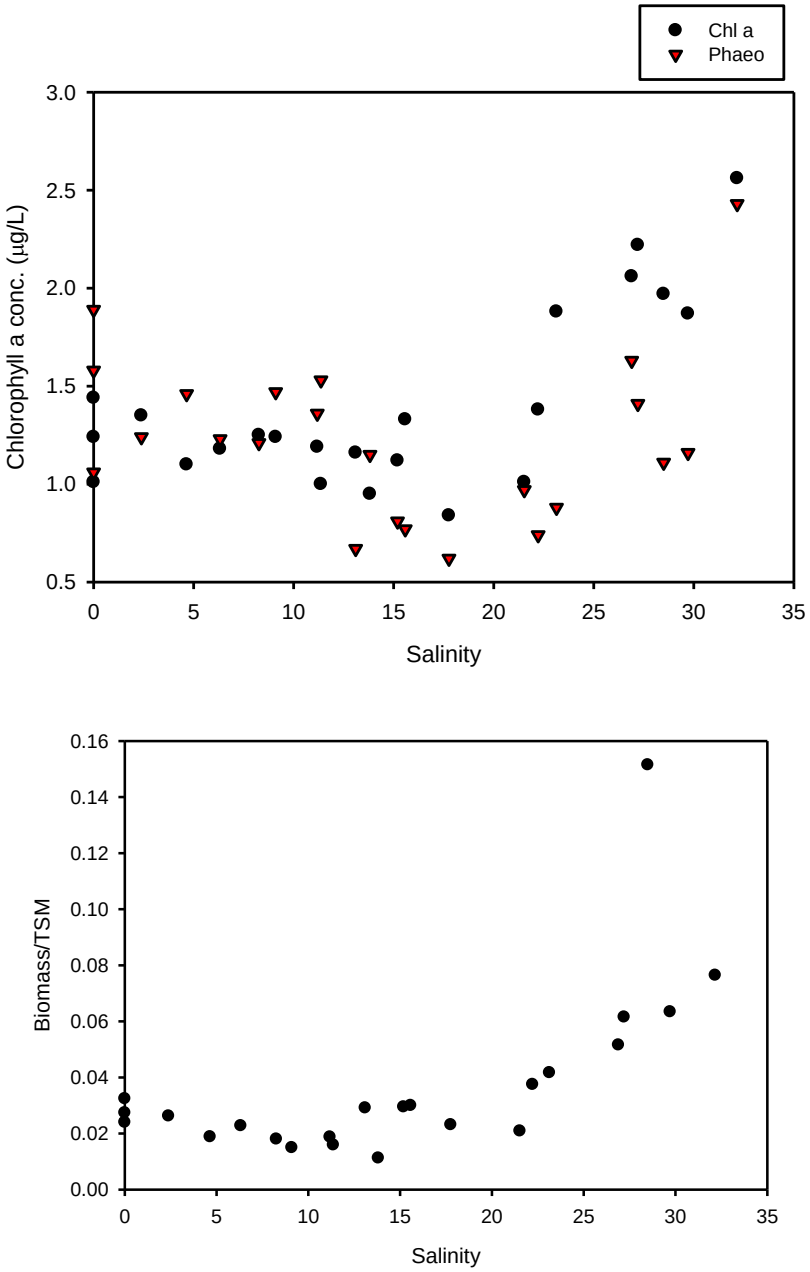


Figure 4-41 **(a) Chlorophyll a (Chl a) and phaeophytin (Phaeo) concentrations and phytoplankton as a function of salinity. Phaeophytin is a degradation product of chlorophyll a and these concentrations are indicative of live and senescent algal biomass. (b) Biomass as a fraction of TSM over the salinity gradient. Data are for a low flow period (November, 1999), and show the increase in algal suspended biomass (live and dead algae) and increasing proportion of biomass in suspended particulates along the salinity gradient.**

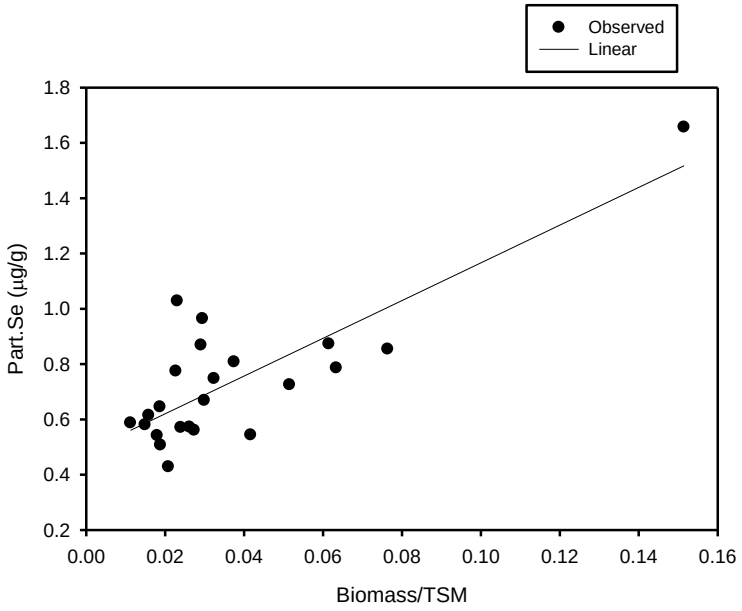


Figure 4-42 Correlation between particulate selenium concentrations and phytoplankton biomass as fraction in TSM (Source: Doblin et al. 2006).

The model-predicted slow changes in particulate selenium concentrations due to changes in dissolved selenium concentrations seem to agree with observed patterns in Doblin et al. (2006). Particulate selenium concentrations for September 1986 seem to be similar to observed concentrations in October 1998 and November 1999 (Figure 4-43), while for this time period refinery loads decreased by 3.85 kg/day and selenite concentrations show a 47% decrease (Figure 4-44).

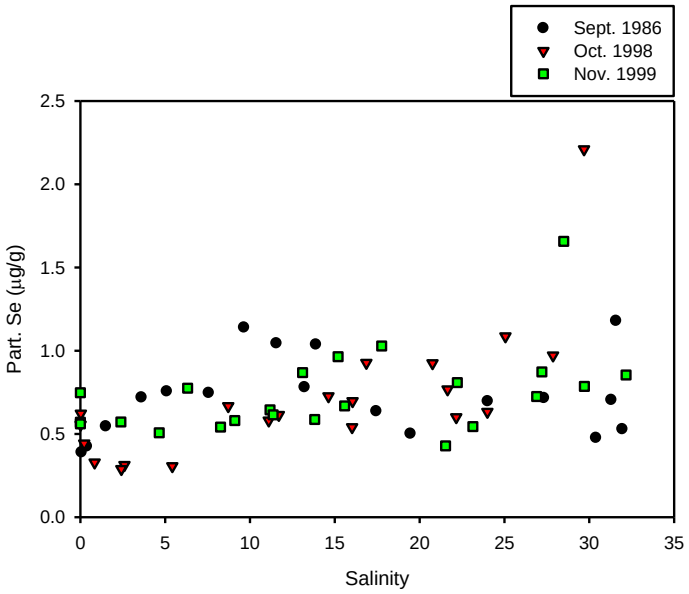


Figure 4-43 Particulate selenium concentrations (in µg/g) under low flow for September 1986, October 1998 and November 1999 (source: Doblin et al. 2006).

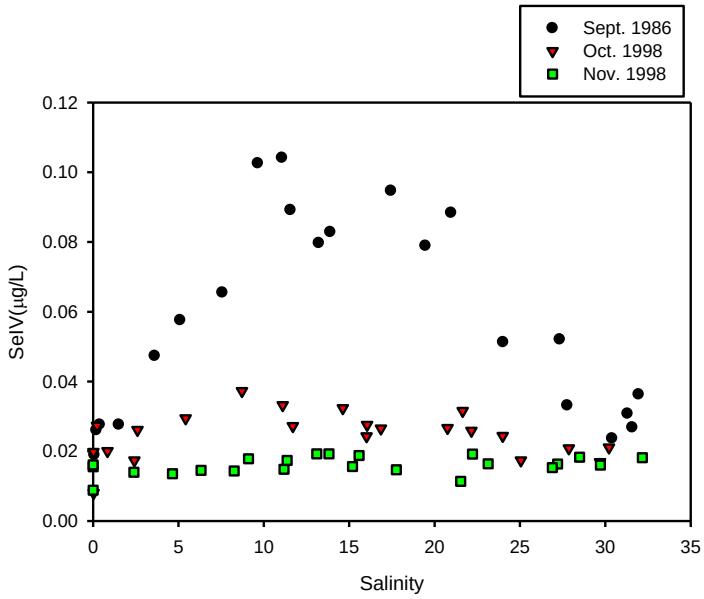


Figure 4-44 Selenite concentrations (in µg/L) under low flow for September 1986, October 1998 and November 1999 (Source: Doblin et al. 2006).

4.9. SUMMARY OF EXPANDED MODEL TESTING

The additional model evaluation presented in Section 4, combined with evaluation of the model against data that were not used for calibration (Section 3), provides confidence in the model formulation, parameterization, and input loads used in this work. The following key features from the modeling work are significant:

- The model is able to capture variation in the dissolved and particulate selenium data, including data at the species level. Not every feature of the observed data are fit, but across a range of dates and hydrologic conditions, the model is able to reproduce average conditions reasonably well. The model also represents average conditions in TSM and chlorophyll a well, although it does not do as well at matching peaks in space and time.
- The model is able to represent ranges of biological selenium data, including data in bivalves and predator species. For bivalves, the model represents seasonal ranges of concentrations well.
- A model hindcast, applied to 1986 conditions, when refinery and San Joaquin River loads were higher than present, performed very well in matching the dissolved and particulate selenium concentrations.
- The model is run using riverine input loads over 1999-2006 that are constructed from data collected in 1999. Even with this simplification, the model is able to represent various features of the annual and seasonal trends in bivalve data, especially when a range of boundary values are used to run the model.

5. MODEL PREDICTIONS

The preceding steps of model calibration and evaluation against new data (Section 3) and testing under an expanded range of conditions (Section 4), set the stage for us to present scenarios where predictions of selenium concentrations in various compartments (dissolved, particulate, sediments, bivalves) are made under imposed load changes. As this TM is being prepared, numeric targets for the TMDL are still not final, and the load scenarios presented in this section are not meant to imply a specific load allocation for the TMDL, but primarily to summarize our understanding of the linkage between sources and various endpoints of interest as embodied in the model. A test is also performed allowing for a consistent increase in San Joaquin River flows to the Delta, to describe a future condition where Delta exports preferentially withdraw Sacramento River water. Finally, for further evaluation of these results, the model predictions for a selected load change scenario are compared against predictions made using the Presser and Luoma (2006) approach.

5.1. LOAD CHANGE SCENARIOS

A series of load-change scenarios were run to evaluate the effects of changing point and non-point sources on the dissolved and particulate selenium concentrations in water and selenium concentrations in bivalves. These scenarios are listed in Table 5-1, and represent scenarios that are within the range of plausibility (e.g., 30-50% reductions) to those that are extreme (such as complete removal of all tributary and point source loads). The goal is to demonstrate the model response under a wide range of conditions.

For performing the model prediction simulations, clam ingestion rates and assimilation efficiencies of different selenium particulate species by bivalves are listed in Table 5-2.

For each scenario, the model provides predictions for all dissolved and particulate species in time and space, as well as concentrations in biota. These calculations are performed over 1999-2006, and, as noted in Section 4, use two sets of particulate boundary conditions, for the riverine and seawater ends, to provide an estimate of the future range of conditions. Example results are shown comparing the base case results to Scenario 2 in Figure 5-1. In this case, the spatial distribution of dissolved selenium and particulate selenium is shown, where each is computed by summing the species-level data. These plots show the response of the dissolved concentration to the change in dissolved load, and the minimal response in particulate concentrations. Also shown in the plots is the response of the particulate concentrations to using different particulate boundary conditions. The particulate boundary conditions have minimal impact on the dissolved concentrations. Temporal results from the base case and Scenario 2 are shown in Figure 5-2 for a specific location in the estuary (Carquinez Strait). The temporal results are consistent with spatial results, in that Scenario 2 results in a change in dissolved-phase concentrations although not in the particulate or bivalve concentrations.

Table 5-1
Load Change Scenarios Tested Using the Model

Scenario	Description	Loading Factors as a Fraction of Base Case Loads, Unless Specified as a Concentration in µg/l[5]							
		Riverine Particulate Selenium Loads			Dissolved Selenium Loads				
		BEPS	PSP	Phyto	Sac.	SJR.	Ref.	Trib.	POTWs
1	Base case	1	1	1	1	1	1	1	1
2	Removal of all point source loads (refineries, POTWs), and local tributary loads	1	1	1	1	1	0	0	0
3	30% reduction in refinery and San Joaquin River loads, dissolved only	1	1	1	1	0.7	0.7	1	1
4	50% reduction in all point sources (refineries, POTWs), local tributaries and San Joaquin River loads, dissolved only	1	1	1	1	0.5	0.5	0.5	0.5
5	Increase dissolved selenium loads from San Joaquin River by a factor of 3, particulate loads remain the same as the base case	1	1	1	1	3	1	1	1
6	Decrease dissolved selenium loads from San Joaquin River by a factor of 50%, particulate loads remain the same as the base case	1	1	1	1	0.5	1	1	1
7	Increase particulate selenium loads associated with PSP, BEPS, and phytoplankton from Sacramento River by a factor of 3, dissolved loads remain the same as the base case	3	3	3	1	1	1	1	1
8	Decrease particulate selenium loads associated with PSP, BEPS, and phytoplankton from Sacramento River by a factor of 50%, dissolved loads remain the same as the base case	0.5	0.5	0.5	1	1	1	1	1
9	Increase San Joaquin River particulate loads by 3x, other loads stay the same	1	1	1	1	1	1	1	1
10	A natural load scenario, where the point sources are zero, the local tributary loads and speciation are at Sacramento River values, and the San Joaquin River is at 0.2 µg/l, at current speciation	1	1	1	1	0.2 µg/l	0	Sac. R. levels	0

[5] Base case loads are not constant through time in the simulations. When a load change is imposed, this means that the entire time series of load inputs is multiplied by the same factor.

Table 5-2
Parameters for DYMBAM Model Used in Model Prediction Simulations

No.	IR, g/g/day	AE (particulate elemental selenium, PSe0), fraction	AE (particulate adsorbed selenite and selenate, PSeivvi), fraction	AE(particulate organic selenide, POrgSe), fraction
1	0.65	0.2	0.45	0.8

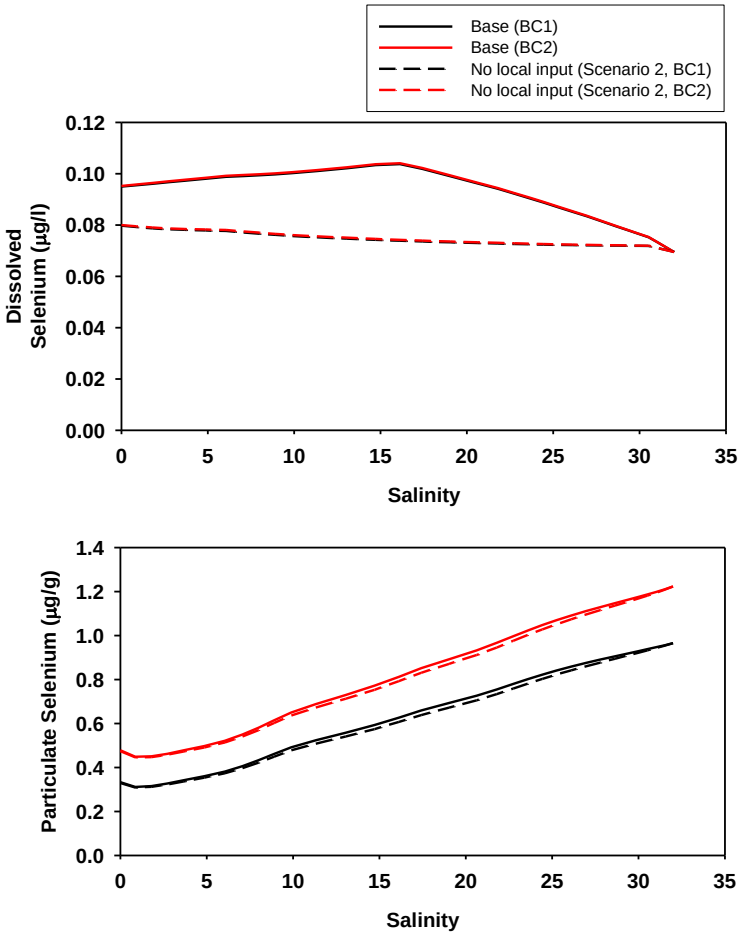


Figure 5-1 **Comparison of base case results with Scenario 2 (no local point source or tributary inputs) for a simulated date of November 11, 1999. Results are shown for dissolved selenium (sum of selenate, selenite, and organic selenide), and particulate selenium (elemental selenium, organic selenide, and adsorbed selenate+selenite). BC1 and BC 2 refer to the higher and lower boundary conditions associated with particulates presented in Section 4. For Scenario 2, the change in loads results in a significant change in dissolved concentrations, which are insensitive to the boundary condition used. Particulate and bivalve concentrations, in contrast, although dependent on the boundary condition used, show no change in Scenario 2.**

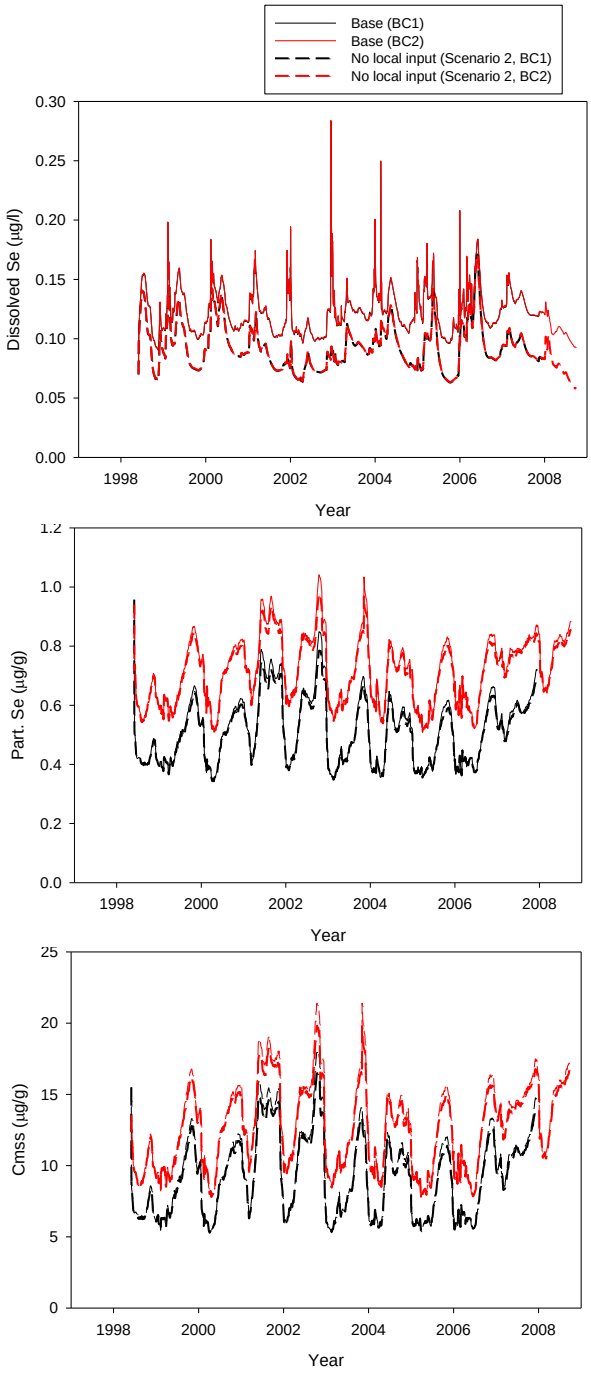


Figure 5-2 **Comparison of base case results with Scenario 2 for Carquinez Strait over 1999-2006. Results are shown for dissolved selenium (sum of selenate, selenite, and organic selenide), and particulate selenium (elemental selenium, organic selenide, and adsorbed selenate+selenite), and bivalves. BC1 and BC 2 refer to the higher and lower boundary conditions associated with particulates. As seen in the previous figure, for Scenario 2, the change in loads results in a significant change in dissolved concentrations, which are insensitive to the boundary condition used. Particulate and bivalve concentrations, in contrast, although dependent on the boundary condition used, show no change in Scenario 2.**

To present the results of the base case plus the nine scenario cases in Table 5-1 (ten scenarios in all), a more compact presentation is used as shown in Figure 5-3, Figure 5-4, and Figure 5-5. These box plots allow side-by-side comparison of scenario results, along with consideration of the two particulate boundary conditions for each scenario. The range of values associated with specific months in the simulation period, representing a wet and a dry year are shown, including the variability computed by the model for the selected month. As in the previous figures, the constituents shown are dissolved selenium (all species), particulate selenium (all species), and bivalve selenium. Data are shown for April 1999 (wet month in a wet year), November 1999 (dry month in a wet year), and July 2001 (dry month in a dry year). The last period represents a condition where selenium uptake and bioaccumulation may be exacerbated due to long residence times.

The following observations can be drawn from the set of scenarios presented here:

- Certain loads, including point sources and local tributary contributions, are considered to be entirely in the dissolved form. When these loads are reduced (Scenarios 2, 3, and 4), there are corresponding decreases in the dissolved concentrations, but minimal change in particulate species concentrations. The overall decrease is nonetheless limited, because the Sacramento River dissolved load, a large, low concentration flow, is not decreased in any scenario.
- The additional variability imposed by using two boundary conditions for particulates is clearly visible in the concentrations calculated for bivalves and particulates.
- Changes in the bivalve concentrations of selenium (expressed as μg/g) follow trends in particulate concentrations, with lower values during a high flow month, and higher values during a low flow month.
- Scenario 5, a tripling of the San Joaquin River dissolved load, has a major impact on dissolved phase concentrations, and a smaller, although still significant, impact on the particulate concentrations.
- Scenario 6, a 50% decrease of the San Joaquin River dissolved load shows limited impact on dissolved and particulate concentrations, in large part because the decrease is swamped by the contribution of the Sacramento River load.
- Scenarios 7 and 8, tripling and a halving of the Sacramento River particulate load only (the dissolved load is unchanged), show a major effect on the particulate and bivalve concentrations (an increase and a decrease respectively).
- Scenario 9, a tripling of the San Joaquin particulate selenium load, with all dissolved loads remaining unchanged, results in an increase in the bay particulate and bivalve concentrations, albeit not as large as change as caused by an increase in the Sacramento River particulate concentrations (Scenario 7).
- Scenario 10, using what might be natural selenium loads in the system, shows a major impact on the dissolved phase concentrations, and a smaller effect on the particulate and bivalve concentrations.
- The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year. This relates to the

lower contribution from the Delta in these periods and the longer residence time in the bay.

Overall, these scenarios provide insight into the representation of the bay in the ECoS model framework, and highlight most important sources that relate to endpoints of interest in the TMDL. They demonstrate the somewhat different behavior of dissolved and particulate selenium over time scales and residence times that pertain to the simulation period, even though it is known that the two phases are inter-related through uptake, mineralization, and adsorption/desorption.

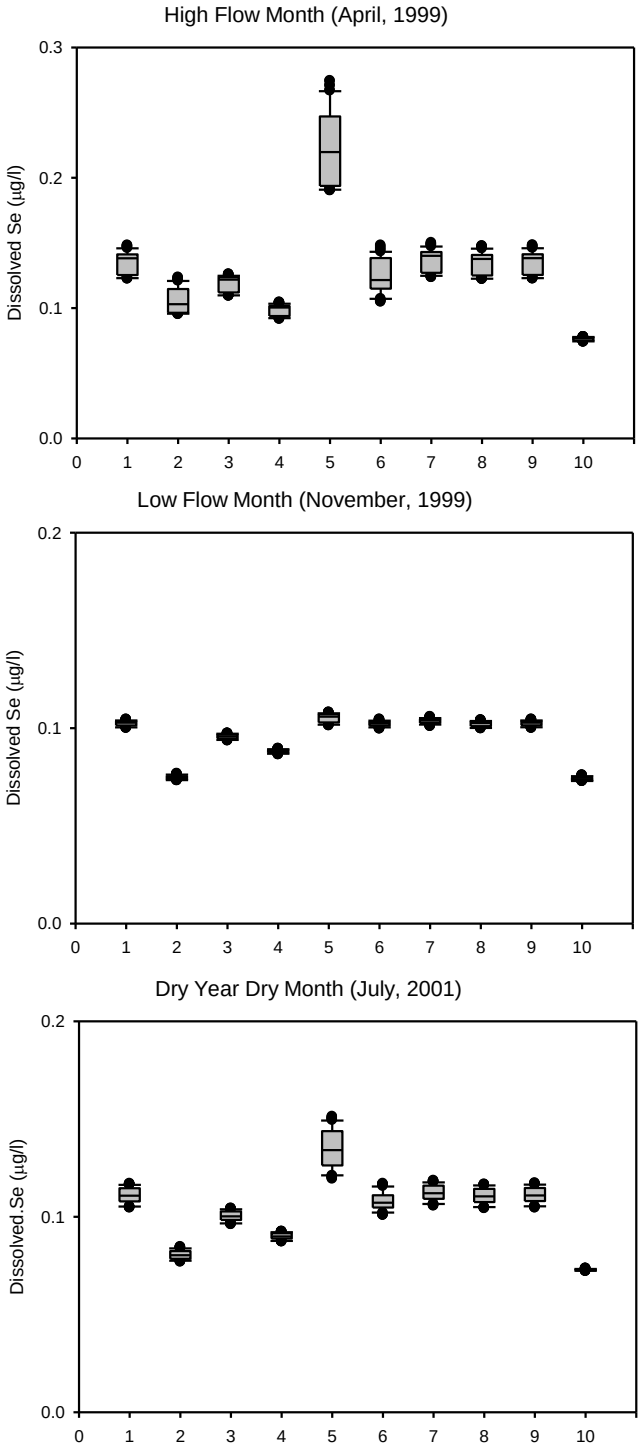


Figure 5-3 **Impacts of Scenarios 1-10 on dissolved selenium concentrations for three months of the simulation period, representing a wet year (1999), and a dry year (2001). The periods shown include a wet month (April 1999), and two dry months (November 1999 and July 2001). The response due to each loading scenario varies by season. Simulated concentrations for Carquinez Strait are compared.**

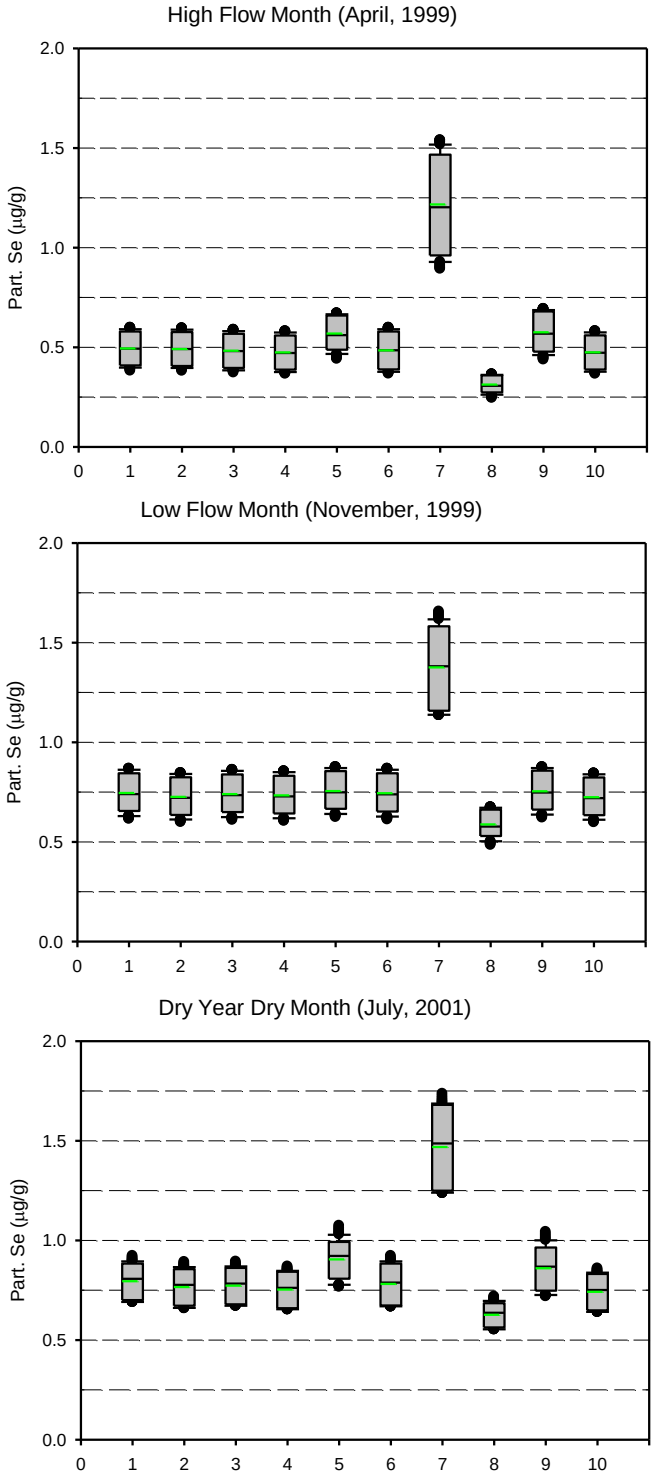


Figure 5-4 **Impacts of Scenarios 1-10 on particulate selenium concentrations for three months of the simulation period, representing a wet year (1999), and a dry year (2001). The periods shown include a wet month (April 1999), and two dry months (November 1999 and July 2001). The response due to each loading scenario varies seasonally, and also shows different behavior from dissolved selenium concentrations, especially Scenarios 5, 7, and 10. Simulated concentrations for Carquinez Strait are compared.**

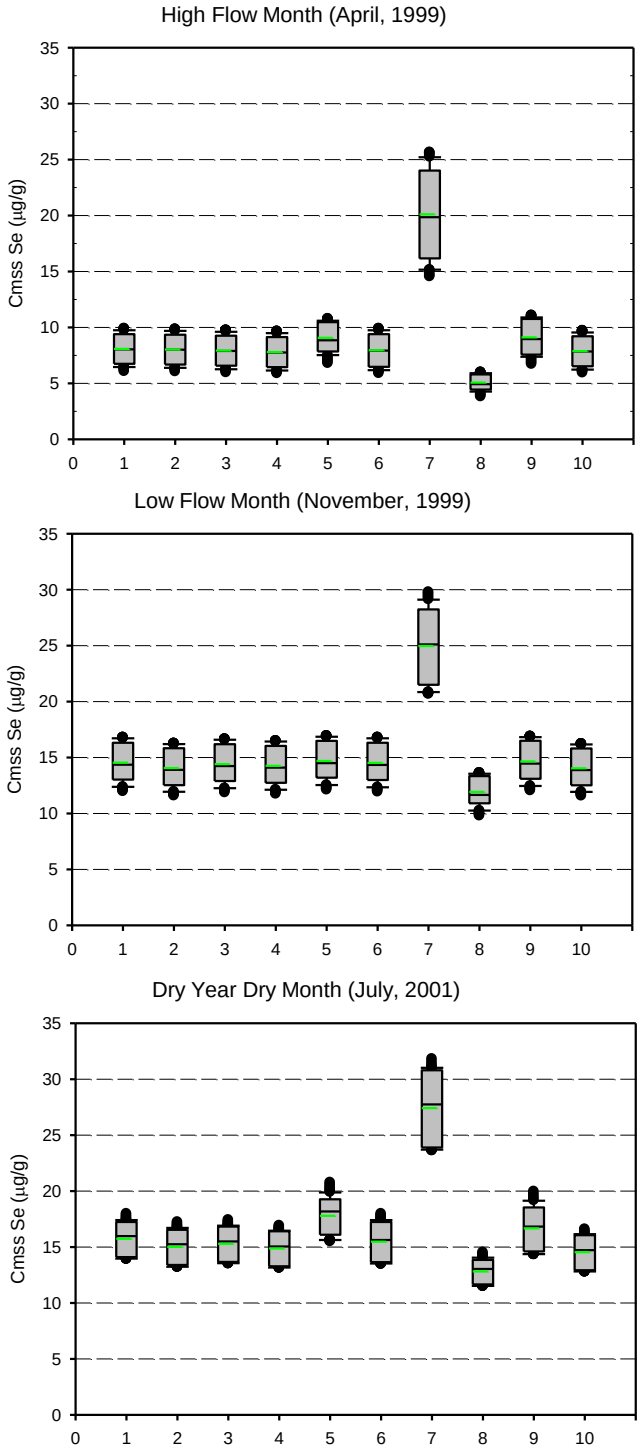


Figure 5-5 **Impacts of Scenarios 1-10 on bivalve selenium concentrations for three months of the simulation period, representing a wet year (1999), and a dry year (2001) for the same seasons as shown in the prior two figures. The response due to each loading scenario varies seasonally, and is correlated with the particulate concentrations. Concentrations are systematically higher during the two dry months shown, and higher concentrations occur in the dry month of a dry year. Simulated concentrations for Carquinez Strait are compared.**

5.2. EFFECTS OF INCREASING SAN JOAQUIN RIVER FLOW

To test the changes in particulate selenium as a result of load changes from the rivers, particularly from the San Joaquin River, the model was run using the same scenario as in Meseck (2002), assuming that all the San Joaquin River flow at Vernalis will reach the Bay. This is in contrast with current conditions, where a significant part of the San Joaquin flow is withdrawn from the Delta into aqueducts. Under the elevated flow condition, the Delta removal effect of selenium was also considered to be lost. Therefore, the scenario assumes elevated inputs of selenium as a result of both increase in flow from the San Joaquin River and the loss of delta removal effects on selenium.

Model simulations using San Joaquin River flow at Vernalis were compared to simulation results using normal San Joaquin River flow (base case). Under the base case, flow from the San Joaquin River was estimated as the difference between Delta outflow and flow from the Sacramento River at Rio Vista. Simulated dissolved and particulate selenium concentrations were higher under the scenario of increased San Joaquin River flow than the base case, for both high flow and low flow periods (Figure 5-6 and Figure 5-7).

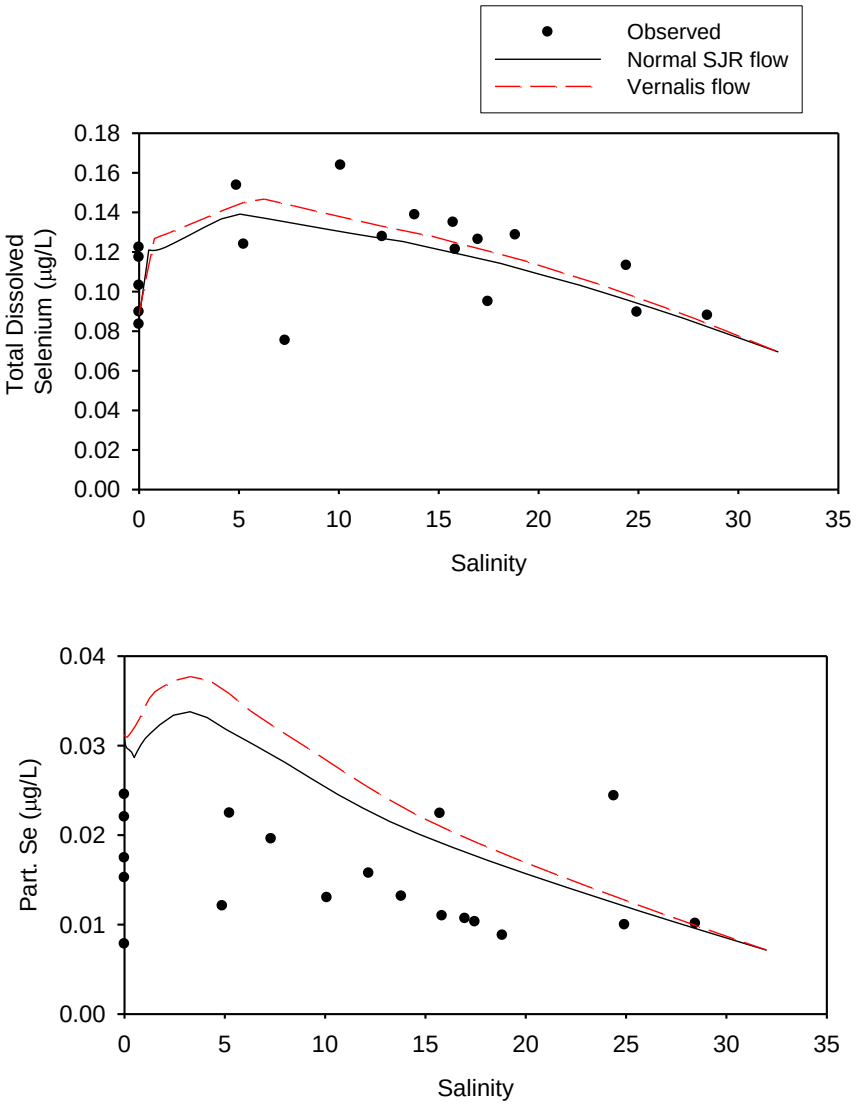


Figure 5-6 **Predicted dissolved and particulate selenium for different San Joaquin River discharge during a high flow period (April 14, 1999).**

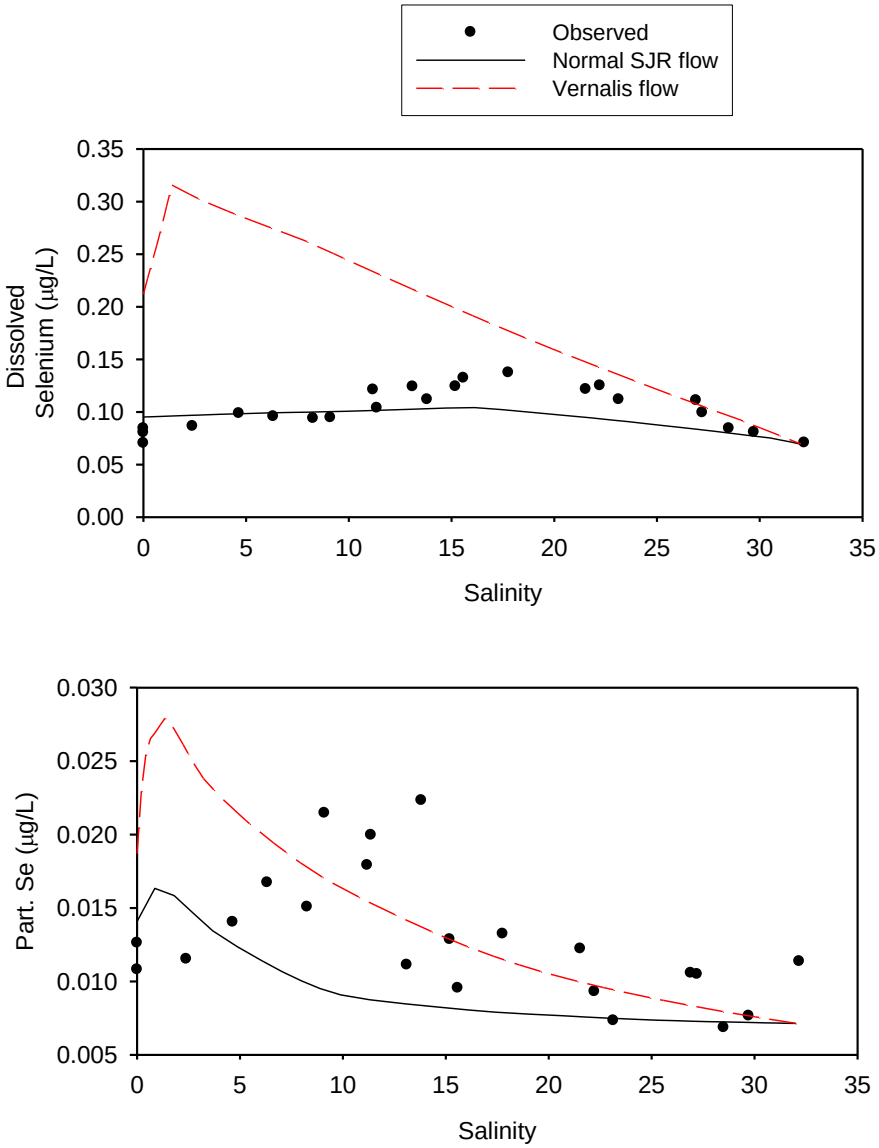


Figure 5-7 **Predicted dissolved and particulate selenium for different San Joaquin River discharge during a low flow period (November 11, 1999).**

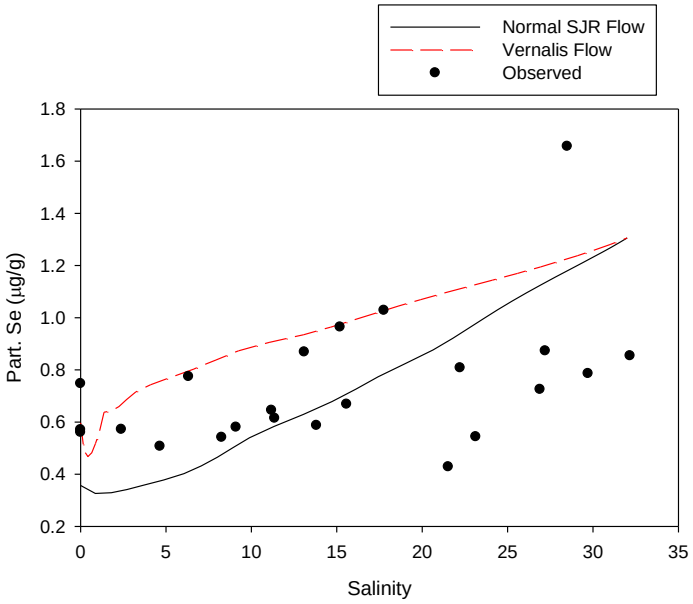


Figure 5-8 **Predicted particulate selenium concentration (µg/g) under estimated San Joaquin River flow at the confluence compared to the prediction for flow at the confluence set to the Vernalis flow rate.**

Predicted model-simulated selenium concentrations on particulates (µg/g) are significantly higher under the scenario of increased San Joaquin River flow, particularly for the upper estuary. Setting the flow of the San Joaquin River to the measured flow at Vernalis, particulate selenium concentrations are nearly doubled with increases greater than 0.4 µg/g predicted in the upper estuary (Figure 5-8).

5.3. COMPARISONS WITH THE PRESSER AND LUOMA (2006) APPROACH

As discussed in more detail in TM-5, the Presser and Luoma model conceptualizes the fate of selenium under various loading scenarios, with an emphasis on sources from the Central Valley, including the San Joaquin River, the Sacramento River, and from petroleum refineries. Concentrations at the head of the estuary are estimated as the flow-weighted average of all influent concentrations as shown in Figure 5-9. Concentrations at Carquinez Strait are half of these values, based on sea-water mixing. Particulate concentrations are estimated using a range of K_d values appropriately chosen for different aquatic environments (1,000, 3,000, and 10,000 L/Kg).

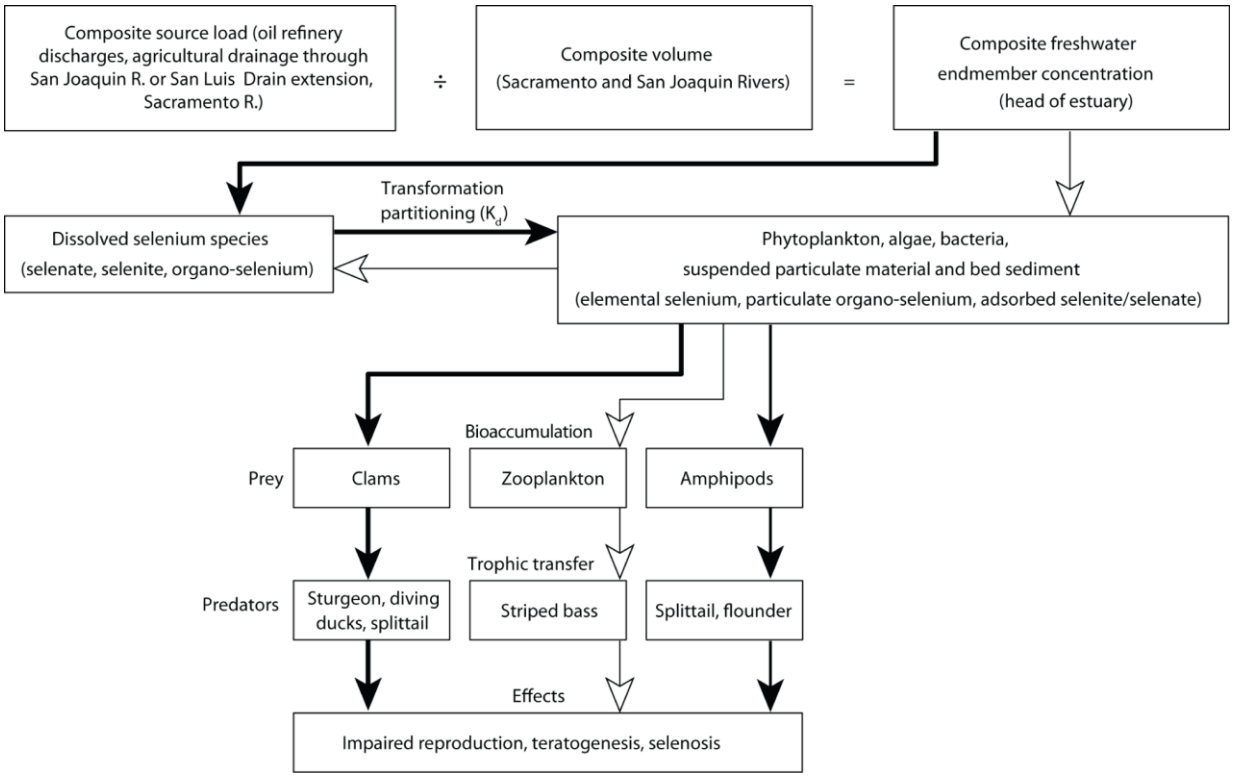


Figure 5-9 Conceptual model describing linked factors that determine the effects of selenium on ecosystems. (from Presser and Luoma, 2006)

Using flow values for different hydrologic periods, this approach can be used to calculate selenium concentrations at the head of the estuary and in Carquinez Strait. An example calculation, building on a wet year, low flow season scenario presented in Presser and Luoma (2006), is shown in Figure 5-10. For this specific scenario, loading from the proposed San Luis Drain was set at zero in the original work.

Source	Flow (million acre-feet)	Se Conc (ug/L)
Sacramento River	2.3	0.04
San Joaquin River	0.5	2.5
Refineries	0.005	50
Selenium concentrations		
Head of the estuary	0.57 ug/L	
Carquinez Strait	0.28 ug/L	
Particulate Selenium		
Kd = 1,000 L/kg	0.57 ug/g	
Kd = 3,000 L/kg	1.70 ug/g	
Kd = 10,000 L/kg	5.68 ug/g	

Figure 5-10. Presser and Luoma (2006) calculations of selenium in the NSFB based on flows and concentrations in the Sacramento River, San Joaquin River, and the refineries.

The approach presented by Presser and Luoma (2006) can also be applied to data employed in these calculations, with the change that some additional sources, notably local tributaries and non-refinery point sources, are identified, and updated concentrations for all sources are used. These calculations are shown in Figure 5-11 and are compared with the ECoS-based NSFB model calculations presented earlier (Scenario 4 in Table 5-1, 50% reduction in all loads except Sacramento River). This plot shows significant differences between the two approaches, especially average values calculated, and the range of concentrations across the salinity gradient. Extending the calculations to particulate selenium (Figure 5-12), we can see a critical difference: the Luoma and Presser approach indicates a particulate concentration decrease for the load reduction embodied in Scenario 4, whereas the ECoS-based approach does not. This response is critical in evaluating the use of these models for the TMDL. The linear response in the Presser and Luoma approach may overstate the anticipated response in particulate concentrations to any changes in load.

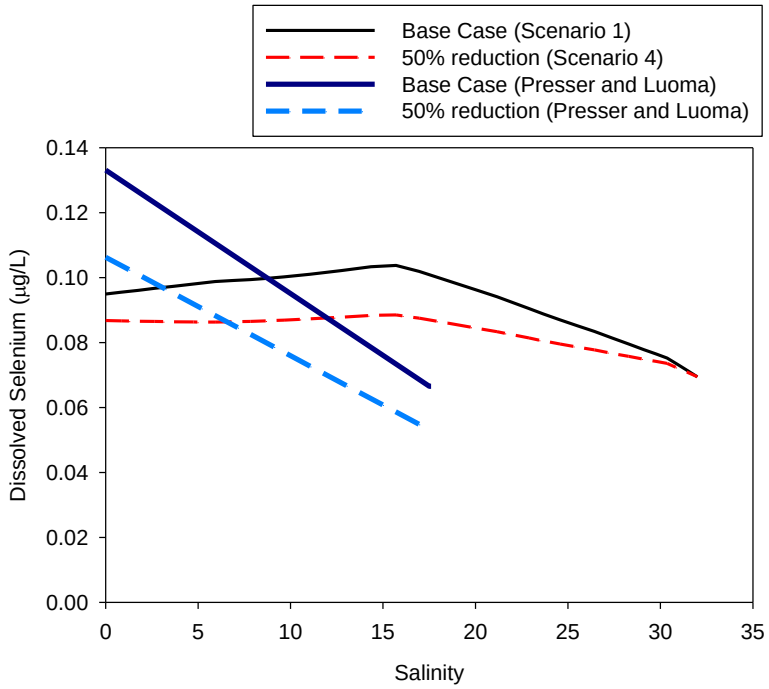


Figure 5-11 **ECoS-based model calculations for load reduction Scenario 4 compared with Presser and Luoma (2006) calculations for the same load reduction. The value in the mid-salinity range corresponds to the division by two employed to reflect sea water mixing at Carquinez Strait in the Presser and Luoma approach. The diagonal lines are shown for comparison with the ECoS-based approach; Presser and Luoma (2006) do not report dissolved selenium for all salinities.**

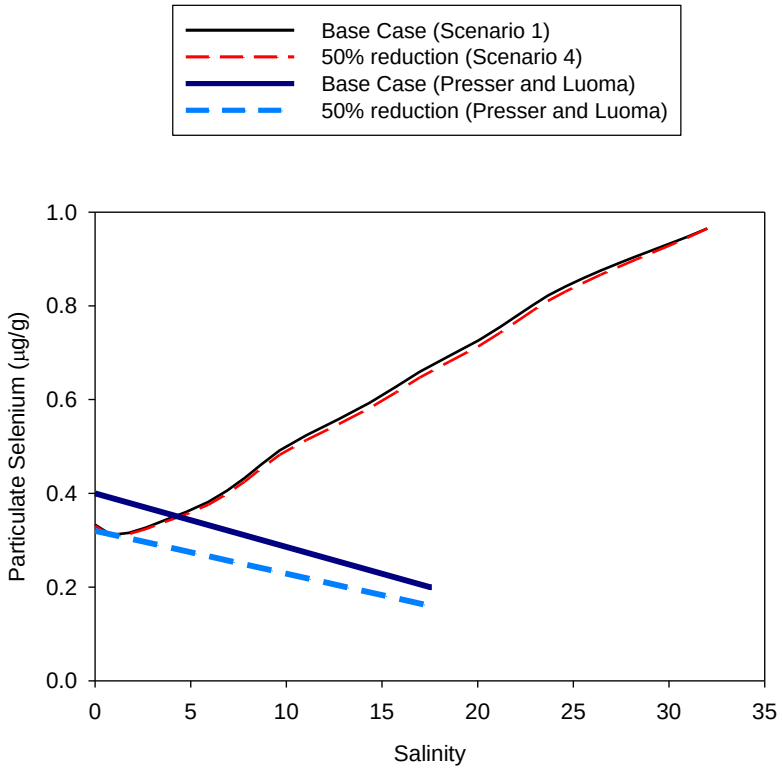


Figure 5-12 **Particulate selenium from ECoS model calculations compared with particulate concentrations using the Presser and Luoma (2006) approach with values of Kd set at 3,000 L/kg. The diagonal lines are shown for comparison with the ECoS-based approach; Presser and Luoma (2006) do not report particulate selenium for all salinities.**

The comparison of the simple and complex models provides an understanding of the strengths and weaknesses of each approach. The Presser and Luoma (2006) model is easy to explain to stakeholders and is relatively transparent, which are clearly valuable assets in a TMDL-setting process. However, the model does not fully capture the processes associated with particulate selenium uptake, which influence the results obtained for load changes from the base case, a feature that is also of importance to the TMDL.

6. DISCUSSION

The preceding sections have detailed the development and refinement of a model of selenium transport and bioaccumulation in North San Francisco Bay. The model is built on previously published work (Meseck and Cutter, 2006; Presser and Luoma, 2006), and extends it in some important ways that directly relate to the selenium TMDL for the bay. This includes detailed characterization of all point and local tributary sources, use of the most recent data for driving the model, detailed characterization of particulate selenium, and inclusion of uptake/bioaccumulation by filter feeders and predator organisms. Below we discuss the application, calibration, and performance of the model, and the key insights derived from this work.

6.1. MODEL INPUTS

The model was run using input data from a variety of sources, not all of which were measured at the same frequency. Important model inputs for which data were generally available over a simulation period of 1999-2006, include flows in the rivers and local tributaries, chlorophyll a concentrations, suspended solids concentrations, salinity, and total selenium in the rivers and point sources. Data on selenium speciation (in the dissolved phase and in the particulate phase) on selected loads (refineries and riverine sources) were available primarily for 1999. When simulations were performed over 1999-2006, the model inputs, for most part, were based on observed data. However, because selenium speciation data was not available beyond 1999, much of the speciation of the input loads was based on 1999 conditions, i.e., the speciation ratios were applied to measured total selenium data. The model input setup thus required some assumptions that, in future, could be addressed through more targeted data collection as discussed below.

6.2. MODEL PERFORMANCE DURING CALIBRATION (1999)

Model calibration involved the selection of the principal transformation rates that pertain to flow, salinity, sediment transport, phytoplankton growth, and selenium chemistry. Many of these values were based on values reported in the scientific literature, although about half the parameters were estimated by adjusting values to fit observed data. The model was calibrated to data primarily from 1999, for which detailed selenium speciation data in the estuary were available.

For the simulation period, the model is able to simulate key aspects of physical and biological constituents that affect selenium concentrations. The model simulates salinity along the estuary well for different hydrological conditions. The evaluation results for phytoplankton and TSM over short-time periods (during specific sampling events for selected years) and long-term periods for multiple years indicated that the model is able to simulate the general temporal and spatial pattern in TSM and phytoplankton, although specific-day peaks may not match very well. For phytoplankton, a few spring blooms are not captured by the model as the model uses a single light limitation function to simulate growth, which limits phytoplankton growth in spring months. Overall, for ancillary parameters, especially TSM and phytoplankton, the model does better at fitting average concentrations than peak concentrations. To some extent this is a consequence of the 1-D formulation of the model, although local variability in driving parameters cannot be ruled out. However, given the hydrodynamic complexities of San Francisco Bay, the inter-annual

and seasonal variability in hydrology, this one dimensional model produces reasonable results of the ancillary variables for use in computing selenium fate and transport.

The simulated selenium species include dissolved forms such as selenite, selenate and organic selenide and particulate species such as adsorbed selenite and selenate, particulate organic selenide and particulate elemental selenium. The transfer of dissolved selenium to particulate selenium is simulated through kinetic adsorption and phytoplankton uptake, and not through equilibrium partitioning. Uptake of selenium by phytoplankton included kinetic uptake of selenite, organic selenide, and selenate, in decreasing order of importance. The uptake rates used in the model simulations are similar to rates used in Meseck and Cutter (2006). During calibration, the model was able to fit the patterns in concentrations of dissolved selenate and selenite well, although it performed less well for dissolved organic selenide. Similarly, the model was able to fit the particulate selenate plus selenite better than the particulate organic selenide. In general the model was better able to represent the general trends in concentration better than the localized spatial variation. The reasons underlying this behavior are not fully understood and may relate to local variability or to small scale processes that are not captured in the 1-D model.

6.3. MODEL PERFORMANCE DURING 1999-2006

Using the 1999 calibrated values for parameters in the model equations, the model was run by varying other inputs over the period 1999-2006. When run in the predictive mode, the model output could be compared with total selenium, which is the only type of selenium data available for years post-1999. This was matched fairly well, although given the degree of aggregation to arrive at this value, it is recognized to not be a strong test of the model.

However, there are other, longer-term data sets for biota to which the model was also applied. The model was able to capture the annual and seasonal variability in clam (*Corbula amurensis*) concentrations fairly well. Although there is less data for comparison, the model also provided reasonable predictions for predator species such as sturgeon and scaup concentrations.

6.4. MODEL PERFORMANCE DURING HINDCAST (1986)

The model was used in a hindcast mode to test predictions in the mid-1980s, where concentrations in many sources, such as the refineries and the San Joaquin River, were higher than at present. The model performed very well at matching the historic data. The results strongly suggest that the transport and transformation of selenium are represented well by the model given its ability to represent different hydrological and load scenarios. For the 1980's conditions, selenite concentrations were higher; however, the particulate selenium concentrations are similar (0.73 μg/g vs. 0.70 μg/g). This indicates that particulate selenium concentrations are not just directly proportional to dissolved concentrations, but are related through processes that may be rate-limited.

6.5. ROLE OF BOUNDARY CONDITIONS ON PARTICULATE SELENIUM

The model testing showed that the selected particulate selenium concentrations at the system boundaries (Sacramento River and Golden Gate Bridge) have a significant effect on the predicted particulate selenium concentrations in the water column and the bioaccumulation of selenium by clams. At the same time there is a lack of particulate selenium concentration

measurements on the Sacramento River where the influence of the selenium concentrations in the Delta are negligible (e.g., at Freeport) and in the near-shore area beyond the Golden Gate Bridge. The data deficiency was dealt with by selecting data available from the nearest suitable stations and, using these measurements, selecting the values of particulate selenium for the boundary conditions that provided the best fit to measured concentrations in the Bay.

The best available data to represent particulate selenium concentrations at the riverine boundary are shown in Table 6-1. The salinity of these samples (near zero) from Rio Vista provides an indication that the influence of the conditions further downstream in the Delta is minimized. The lowest value is this data set is 0.357 μg/g.

Although the data to characterize the boundary values are limited, data in the bay provide another constraint for the model calibration effort. For the riverine boundary condition at Rio Vista, exploratory runs were performed where particulate selenium varied over a wide range (about 0.2 μg/g to 1.4 μg/g in PSP, Table 4-3). If concentrations at Rio Vista were set at the lowest values in Table 4-3, the water column particulate concentrations could not be matched by the model. The range of plausible values for the Rio Vista boundary is therefore more narrowly constrained by the water column values in the bay.

Table 6-1
Rio Vista Particulate Selenium Concentrations (Source: Doblin et al., 2006)

No.	Date	Salinity	Particulate Selenium (μg/g)
1	11/5/97	0.56	0.55
2	6/16/98	0.011	0.357
3	10/7/98	0.017	0.555
4	11/4/99	0.00	0.747

To reflect the uncertainty in the boundary conditions, all simulations were performed with a range of riverine boundary values, albeit not as wide as the one used for exploratory testing in Figure 4-16; the range varied between 0.46 and 0.75 μg/g at Rio Vista.

The particulate selenium concentrations used in the analyses presented in this report are higher than what would be measured in a relatively uncontaminated system, however, this is the range that was consistent with in-bay concentrations. It is clear that there is a need for the best possible characterization of the boundary conditions, especially of particulate selenium, a parameter not always measured in routine monitoring in and around the Delta. The accurate characterization of the particulate concentrations at the boundaries of the system through field sampling efforts is essential to verify the results of this model simulations presented in this report.

6.6. MODEL PREDICTIONS FOR LOAD REDUCTION SCENARIOS

Several illustrative load reduction scenarios were presented to illustrate the relationship between sources and endpoint concentrations (dissolved, particulate, and bivalve concentrations). These load reductions are not proposed TMDL allocations but were meant to provide further insight into the estuary behavior as embodied in this model.

All scenarios consider that the Sacramento River dissolved concentrations are at a regional background level, and that dissolved loads from this source are not modified. Further, boundary values of particulate concentrations for Sacramento River are represented as a range reflecting the uncertainty in this input. For suspended particulates the range in concentrations was 0.46 to 0.75 µg/g, and for bed exchangeable particulates, the range was 0.25 to 0.5 µg/g. Phytoplankton selenium concentrations were expressed as a Se:C ratio, and set at 15.9 µg/g at the riverine boundary.

With the Sacramento River dissolved concentrations setting the floor, changes were made to dissolved selenium loads from refineries, POTWs and other point sources, local tributaries, and the San Joaquin River. Concentrations were changed separately for the particulate load originating from the Sacramento and San Joaquin Rivers. Although the dissolved and particulate loads were treated separately for the purpose of the load scenarios, once in the estuary, the forms are interrelated through the equations for uptake, mineralization, and adsorption/desorption. However, these transformations are rate limited, with literature or calibrated values of rate constants as detailed in Sections 3 and 4, and given the residence times in the estuary, the uptake rates provide a limit to how fast forms of selenium can change from dissolved to particulate and vice versa. Therefore, the rate-limited formulation results in somewhat different behavior for dissolved and particulate concentrations in the scenarios tested.

When dissolved loads, including point sources and local tributary contributions, are reduced, there are corresponding decreases in the dissolved concentrations, but minimal change in particulate species concentrations. The exception is for a tripling of the San Joaquin River dissolved load: this has a major impact on dissolved phase concentrations, and a smaller, although still significant, impact on the particulate concentrations. In comparison, a decrease of the San Joaquin River dissolved load shows limited impact on dissolved and particulate concentrations, in large part because the decrease is swamped by the contribution of the Sacramento River load. A modification of the scenario with the tripling of the San Joaquin River dissolved load (imposed by changing the concentration, but holding the flow the same as the base case) was performed by allowing delivery of Vernalis-level flows directly to the delta, with no attenuation due to aqueduct withdrawals. This resulted in a similar increase in dissolved and particulate selenium concentrations in the bay.

A tripling and a halving of the Sacramento River particulate load only (the dissolved load was unchanged), showed a major effect on the particulate and bivalve concentrations (an increase and a decrease respectively), and highlights the critical role played by this input, and the need for it to be characterized accurately. This load is different from the other loads in that it is not likely to be modified through specific actions; however, given its importance, it is poorly characterized over the period of the simulation.

Complete reductions in the refinery, POTW, and local tributary loads (Scenario 2), result in decreases in dissolved concentrations under the different flow conditions evaluated. However, the associated particulate concentration changes and clam concentration changes are small. Of the three hydrologic periods considered, the difference was slightly larger for the dry flow month in a dry year, but in all cases the difference as a result of this load reduction was smaller than the simulated variation in the base case.

The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year, i.e., for a given load change factor, greater change is observed during the dry periods. This relates to the lower contribution from the Sacramento River during these periods and the longer residence times in the bay. This highlights the need for focusing on dry periods during which the impacts to the bay may be more easily observed.

Overall, these scenarios provide insight into the representation of the bay in the ECoS model framework, and allow evaluation of the underlying model formulation presented here. They demonstrate the somewhat different behavior of dissolved and particulate selenium over time scales and residence times that pertain to the simulation period, even though it is known that the two phases are inter-related through uptake, mineralization, and adsorption/desorption. In this regard, the model formulation is distinct from the Presser and Luoma (2006) formulation that relates dissolved phase concentrations to particulate concentrations through equilibrium-type partitioning, with dissolved concentrations changes causing immediate and proportional changes in particulate concentrations.

6.7. COMPARISON WITH A SIMPLER MODEL

The model computations of dissolved and particulate selenium could be compared with a somewhat simpler published approach based on linear partitioning between dissolved and particulate phases (Presser and Luoma, 2006). The comparison of this simple approach and the more complex ECoS-based approach highlights the strengths and weaknesses of each. The Presser and Luoma (2006) model is easy to explain to stakeholders and is relatively transparent, which are clearly valuable assets in a TMDL-setting process. However, the model does not fully capture the processes associated with particulate selenium uptake, which influence the results obtained for load changes from the base case. In the linear partitioning approach a reduction in dissolved concentrations results in a proportional reduction in particulate concentrations, a result that is different from the ECoS dynamic uptake/mineralization approach. Data from the mid-80s to the late 90's are supportive of the latter, with decreases in dissolved concentrations not causing observable decreases in particulate concentrations. This feature is also of importance to the TMDL. .

6.8. UNCERTAINTIES AND DATA NEEDS

A modeling study, such as the one reported here, provides an opportunity to synthesize information from the system, and in doing so, highlights unknowns that may have a bearing on model predictions. Despite the large amount of data on selenium and its biological uptake in NSFB, there remain significant unknowns that need to be addressed through continued monitoring, as part of future phases of the selenium TMDL. These unknowns are discussed below, and need to be considered during the development of the Implementation Plan for the TMDL. The importance of selenium in the NSFB and the complexity of its behavior are strongly indicative of the need for an active research program in the bay to track these issues.

- **Selenium speciation data:** It is recommended that selenium speciation data for dissolved and particulate selenium along the salinity gradient of the estuary to be collected, at least for a high and low flow year. Particulate selenium speciation at the head of the estuary (e.g., Sacramento River at Rio Vista and San Joaquin River) are

important parameters that need to be sampled under different flow conditions. Such sampling should be conducted each year, with a periodic review of in-bay processes affecting selenium concentrations. Of the particulate forms of selenium, the size ranges that can be ingested by bivalves are of most interest (2-100 µm), and should be considered during the monitoring.

- **Selenium loads:** Selenium loads for different species from the Delta and tributaries remain a large uncertainty, and the vast majority of currently reported measurements are not speciated, and reported as total or dissolved selenium. Dissolved and particulate selenium data with detailed speciation after refinery clean-up are only available for 1999. After 1999, all the available selenium data are in total and dissolved selenium concentrations. Using equations derived for different species of selenium for the Sacramento River at Freeport and San Joaquin River at Vernalis gave good predictions in dissolved selenium concentrations in the Bay. However due to the complexity of the Delta system and the potential transformations occurring in the Delta, selenium loads from the Delta remain uncertain. Riverine inputs of selenium have a large influence on the dissolved and particulate selenium concentrations in the Bay as shown in the sensitivity analysis (Table 4-1). Loads from local tributaries are more significant during high flow than low flow. Uncertainties remain in selenium concentrations and speciation in the tributaries.
- **Selenium transformations:** Transformations of selenium from dissolved to particulate phase through adsorption and phytoplankton uptake are studied less well in marine water than freshwater. There are also uncertainties associated with phytoplankton species with location and time. Seasonal variations in phytoplankton species and selenium uptake by various species of marine phytoplankton are uncertain, as most of the studies were done in freshwater or in the Delta. Cellular selenium concentrations have been reported for some marine phytoplankton species but not all species common in the NSFB.
- **Role of phytoplankton and bacteria in selenium uptake:** Due to limited knowledge on benthic bivalve and zooplankton abundance, the temporal and spatial variability of benthic and zooplankton grazing rates is not well known. The phytoplankton growth formulation, driven by light limitation, uses a single equation across the bay which may not fully represent temporal and spatial variability. It is also recommended that uptake of dissolved selenium by dominant species of phytoplankton and bacteria be studied under the ambient selenium concentrations of the NSFB.
- **Bioaccumulation into the higher trophic levels (fish and birds):** Uncertainties are associated with feeding patterns of the predators due to the migratory nature of certain species (such as surf scoter). Data with good correspondence of time and space in bivalves and predators are sparse. Where dietary concentrations and tissue concentrations can be measured simultaneously, derivation of TTFs can be an appropriate strategy from a modeling standpoint.
- **Sediment deposition and erosion processes:** Sediment deposition and erosion in the NSFB are complicated processes with many unknowns. Deposition and erosion rates can vary significantly over space and time. Erosion can be driven by flow, wind

and tides. Sediment properties (cohesive and non-cohesive) can also affect erosion and deposition. The constructed model currently applied a uniform sediment deposition rate throughout the Bay. The model evaluation results for TSM were considered reasonable for the current selenium TMDL application.

7. Potential Use of the Model in the Selenium TMDL

The calculations described in the preceding pages are the synthesis of a great deal of data and modeling, which was conducted by other researchers over more than two decades. Despite the enormous amount of research attention devoted to selenium in NSFB over this time—as compared to other contaminants for which TMDLs in the region have been developed, such as PCBs and mercury—there still remain some gaps in understanding. At a simple level, one can see these gaps in the calibration and model evaluation figures presented in Section 3, where the behavior of many constituents has not been captured fully, especially when looked at a day-to-day level.

The question for regulators and for developers of the NSFB selenium TMDL is this: Is the model, as presented here, an appropriate tool to further consider in developing load allocations, and monitoring and implementation strategies? Or, are there better ways of representing the system for this TMDL?

It is clearly possible that future development with a more spatially detailed framework and with more detailed characterization of ancillary constituents, such as suspended materials and phytoplankton, may provide a better capability to represent concentrations than has been done in Section 3. Many of these modeling efforts for suspended materials, hydrodynamics, and chlorophyll a, have been ongoing for many years. Although it is feasible to revisit the selenium issue in the future with these calibrated models in hand, it may not occur in the time frame of the selenium TMDL. However, there are data limitations that constrain the potential of future models to fundamentally alter the representation of selenium in NSFB. In particular, adequate calibration of a more detailed selenium model would also require more detailed species level data to be collected in NSFB. Such data have not been collected for nearly a decade, and support for any detailed modeling effort must be contingent on a parallel data collection effort. In the absence of new detailed data, modeling alone may be unlikely to greatly advance the understanding presented here.

The other modeling approach, from a TMDL perspective, is to simplify the system, and treat all sources as entering the head of a well-mixed box, as done by Presser and Luoma (2006). This method has its strengths, not least of which is the ability to communicate the information widely, and to provide a tool where scenario calculations can be rapidly performed on a spreadsheet. This is especially helpful in a regulatory setting where calculations and scenarios need to be evaluated by multiple stakeholders. However, this approach makes other simplifying assumptions, such as treating all selenium species the same way, and estimating particulate selenium with a range of equilibrium partitioning coefficients, that may not reflect our current understanding of behavior in the system. In particular, simulations that we have performed in this report show that influent load reductions, while making changes in the dissolved concentrations in NSFB, have minimal effects on particulate selenium concentrations that are key to the bioaccumulation processes. This finding is driven by the importance of Sacramento River particulate loads in this model, which set a floor for the concentrations observed in the bay. Large load reductions in all non-Sacramento River loads have a limited impact, because the Sacramento River particulate concentrations are still dominant component. However, significant load increases can result in higher particulate concentrations (µg/g) in the bay, and are a possibility that

must be considered in TMDL given proposed flow changes in the Delta. Thus, higher flows and therefore loads from the San Joaquin River can reach the bay with the likelihood of higher particulate concentrations, and adverse impacts to the foodweb that depends on benthic filter feeders. Another finding from the modeling, not entirely represented in terms of total particulate selenium, is that efforts to reduce phytoplankton-associated selenium may be more effective at achieving lower concentrations in bivalves because of the relatively high efficiency with which they are assimilated into bivalve tissue.

Given this background, it would appear that there is a role for use of the currently developed ECoS-based NSFB selenium model in subsequent analyses to be performed by the Regional Board. The analyses that the ECoS-based model could be used for include: development of various load allocation scenarios, for specific numeric targets in fish and development of monitoring strategies to better fill data gaps, such as the limited knowledge of selenium behavior in the Delta. The model can also be used to explore system responses when conditions are very different from current conditions, with higher phytoplankton concentrations, or more extreme dry periods, for example.

To the extent feasible, analyses using this model should be supplemented by other approaches, such as that of Presser and Luoma (2006), and/or other modeling studies that relate to ancillary constituents of relevance to selenium, such as phytoplankton and suspended sediments, as well as other more focused toxicological studies than consider the biological uptake of selenium from bivalves to prey organisms and the internal transport to specific target organs of greatest concern, such as the liver or ovaries (Linville, 2006). Further, these analyses need to be supplemented by more empirical data evaluation approaches, including a "trial and error" approach over an extended period of time, where changes in selenium levels in various biotic and abiotic compartments are closely observed while there are changes in external loading to NSFB from point and non-point sources. The empirical analysis may provide additional insight into possible approaches for attaining selenium targets in NSFB biota.

Irrespective of the use of the model in the TMDL, the study has provided an opportunity to gather and analyze a large amount of data from the system and the watersheds that drain into it. This data analysis has identified gaps, discussed previously, that should be addressed in future phases of the TMDL. However, the following general findings are strongly supported by the analysis presented here, including information in the source analysis for selenium (Tetra Tech, 2008a) and the conceptual model of selenium (Tetra Tech, 2008b) that form the basis of the modeling.

- The major riverine inflows to NSFB (Sacramento and San Joaquin) form the main loads of dissolved selenium. However, dissolved concentrations in the Sacramento River are a tenth of those in San Joaquin River (~0.07 µ/l compared to ~0.7 µ/l). Sacramento River flows are typically several times larger, and the dissolved load contributions from both sources to the Delta are of similar magnitude.
- Particulate selenium concentrations in the riverine flows were directly measured for a limited number of dates. In the Delta, near the Rio Vista boundary of the model and just downstream, the particulate concentrations are ~0.4-0.5 µ/g. These numbers

are elevated further in the estuary with increasing organic fraction in the particulate phase.

- The pathway of most concern from the standpoint of selenium bioaccumulation is the transfer of selenium from particulates to bivalves and the predator species that consume these bivalves.
- The selenium source of most concern in the bay is particulate selenium, which is largely supplied by the riverine loads. Selenium in the water column in the dissolved form may be converted to particulate forms, through phytoplankton uptake and adsorption, but the transformations are highly species specific: selenate interacts minimally with particles, whereas both selenite and organic selenide are more reactive. Should future efforts be focused on the derivation of a partitioning coefficient, or K_d, for selenium, the emphasis must be on deriving species-specific values. If a net K_d is estimated, representing all species of selenium, the value is highly variable depending on the season and flow conditions driven by changing selenium species in the bay.
- The bioaccumulation analysis presents a focused and possibly incomplete evaluation of the adverse effects of selenium uptake on fish and bird species that are benthic feeders. The bivalves chosen for examination in this work, Corbula amurensis, are very efficient at bioaccumulating selenium, more so than other bivalve species. In the bioaccumulation analysis, it is assumed that the predator species, white sturgeon and diving ducks, feed exclusively on this bivalve species. Additionally, the prediction of tissue concentrations in white sturgeon and diving ducks does not take into account the observed seasonal differences in bivalve selenium concentrations. The current assessment of risk to predator species in the bay from selenium uptake is largely a result of the presence of Corbula amurensis, despite the two-decade long efforts to control non-point sources in the Central Valley and point sources in the bay.
- From the standpoint of managing the selenium impacts to the identified biota in the bay, the most effective option is to control the particulate concentrations, which may not be related in a linear manner to dissolved concentrations. Data from mid 1980s and late 1990s show that large reductions in point source loads decreased dissolved phase concentrations, but had a minimal impact on particulate concentrations.
- The modeling also shows that while decreases in particulate concentration (in µg/g) may be difficult to achieve, increases in concentration are possible, should there be increased loads from the San Joaquin basin by means of higher flows into the Delta. Given the range of modifications that are being proposed for the Delta waterways to improve water supplies for export, the likelihood of increased concentrations should be actively considered in the TMDL process.

8. REFERENCES

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APPENDIX 1: CIMIS STATIONS

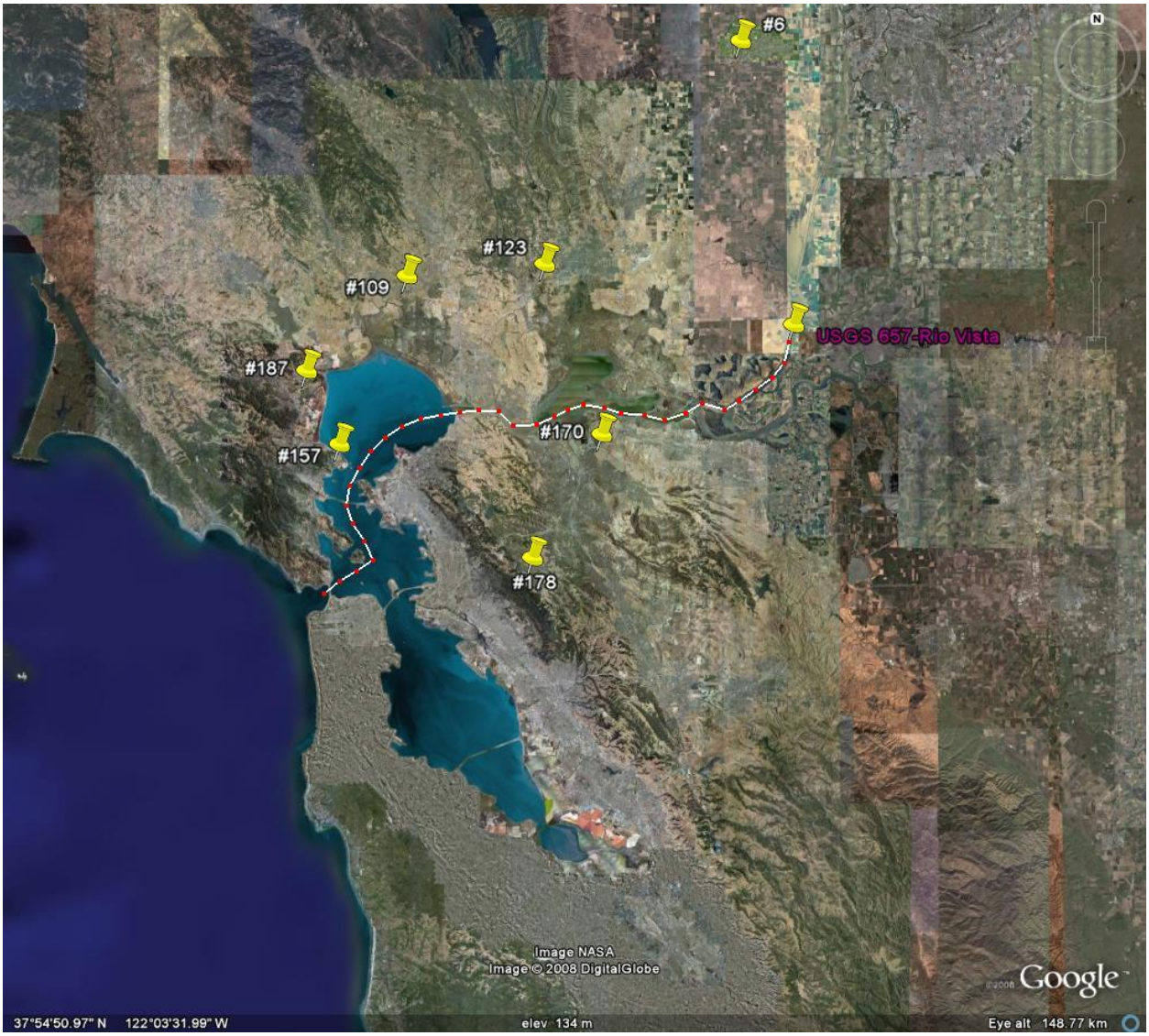

Figure A.1-1 Locations of California Irrigation Management Information System (CIMIS) meteorological stations in the NSFB.

APPENDIX 2: EQUATIONS USED TO SIMULATE ZOOPLANKTON GRAZING

The zooplankton grazing rate is simulated by the model using zooplankton biomass and a modified Ivlev function that predicts the ingestion of phytoplankton per animal (Cloern et al., 1985). The following equation from Meseck (2002) was used:

$$F = 9.5 \times 10\text{-}4 * W\text{^}0.8* e\ 0.069*(T\text{-}10) * (1\text{-}\ e\text{-}0.01*C) \quad \text{(A.2-1)}$$

where T is the temperature (ºC), W is the zooplankton weight (µg C/animal), and C is the biomass of phytoplankton (mg C/m3). The weight of the zooplankton varies from 7 to 63 µg C/animal.

The total daily zooplankton ingestion, I (mg C/m3) is calculated using:

$$I = F * Z \quad \text{(A.2-2)}$$

where Z is the average zooplankton abundance (#/m3).

The specific loss of phytoplankton per day by zooplankton grazing (G) is simulated from Cloern et al. (1985)

$$G = -\ln (B\text{-}I)/B \quad \text{(A.2-3)}$$

with B being the phytoplankton biomass in units of carbon.

Using the equation above resulted in zooplankton grazing rate as high as 0.45/day under chlorophyll a concentration of 2 µg/L, temperature of 15 ºC, and zooplankton weight of 13 µg C/animal. The estimated zooplankton grazing rate is high compared to literature values of 0.01-0.1/day in the bay (Cloern et al., 1985).

APPENDIX 3: EVALUATION OF LEAST SQUARES METHOD

The fitting program used in the model calibration modifies parameter values iteratively, attempting to minimize the sum of square deviations (SSD) from the observed values. To evaluate the effect of starting values in resulting calibrated parameters, SSD values obtained from the calibration process for several parameters are shown in Figure A.3-1 to Figure A.3-5. SSD as a function of different initial values (starting values) for several parameters including dispersion coefficient, scaling factor in simulating velocity of BEPS, San Joaquin River loading constants for organic selenide and selenate, and particulate organic selenide and particulate selenite and selenate are shown. The results indicate that even with different initial parameter values, a similar minimum SSD and calibrated parameter value were reached. This suggested that only one single set of parameters is derived through model calibration and is used in model predictions. The derived value with the lowest SSD was taken as the final calibrated value. The range of SSD was determined by the parameter calibrated (e.g. larger for salinity, in psu and lower for TSP, in g/L).

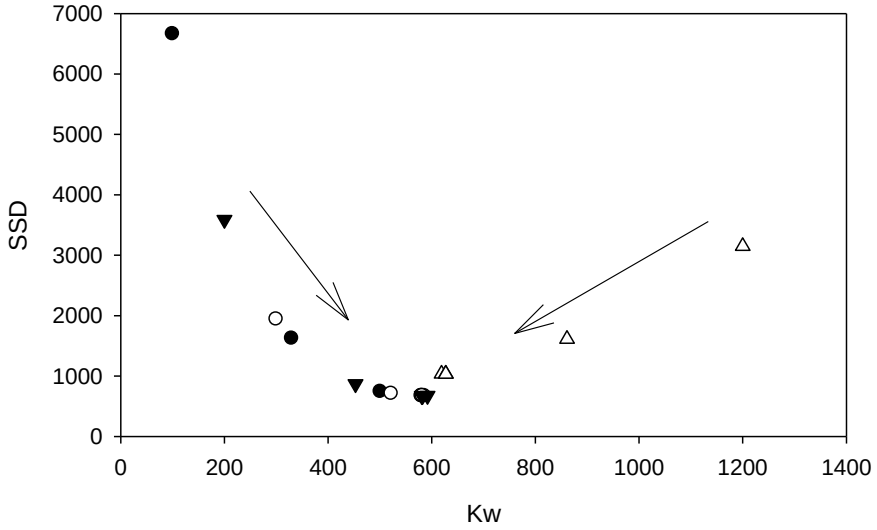

Figure A.3-1 Sum of square deviation as a function starting values in dispersion coefficient. Different symbols represent calibration with different starting values.

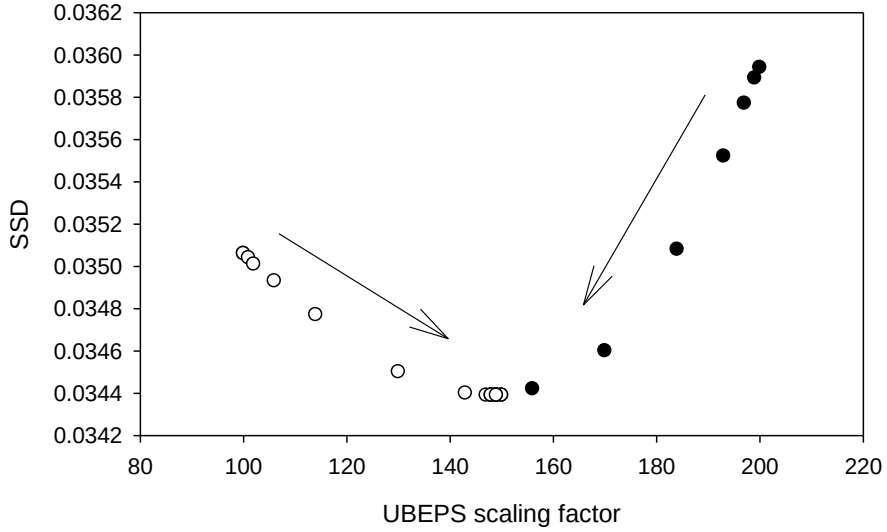

Figure A.3-2 Sum of square deviation as a function of starting values in scaling factor in BEPS. Different symbols represent calibration with different starting values.

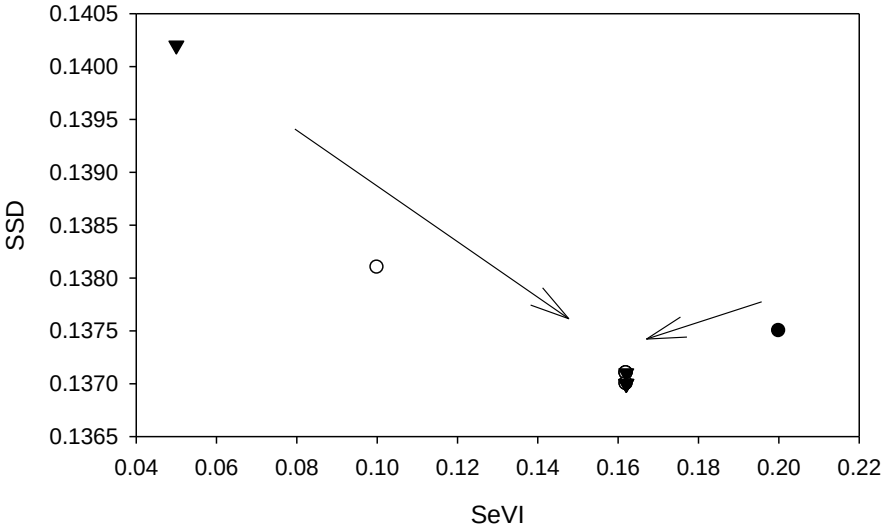

Figure A.3-3 Sum of square deviation as a function of initial values in delta loading constant in selenate. Different symbols represent calibration with different starting values.

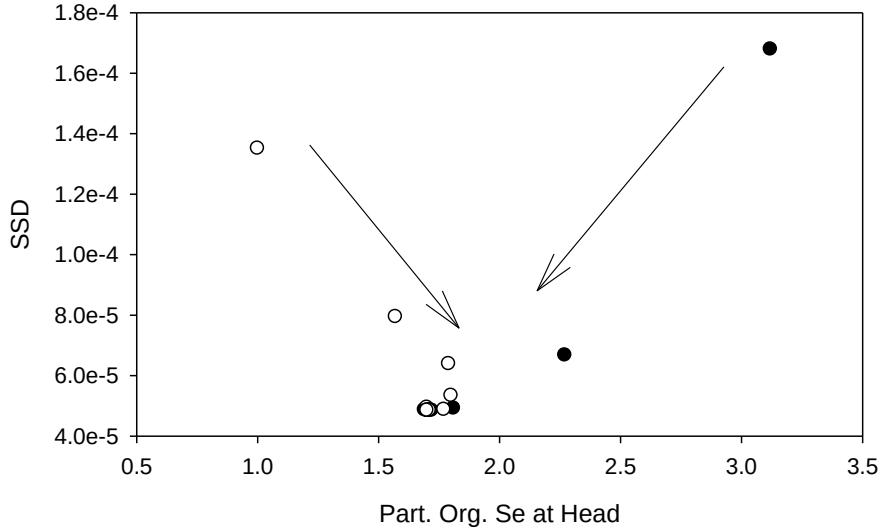

Figure A.3-4 **Sum of square deviation as a function of initial values in particulate organic selenide concentrations at head of estuary. Different symbols represent calibration with different starting values.**

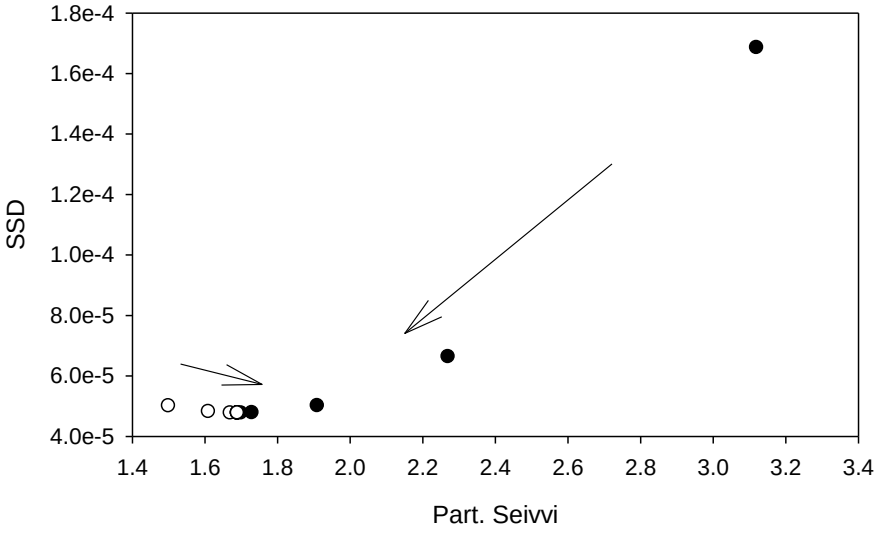

Figure A.3-5 **Sum of square deviation as a function of initial values in particulate selenite and selenate concentrations at head. Different symbols indicate different initial values.**

APPENDIX 4: RELATIONSHIP BETWEEN DISSOLVED AND PARTICULATE SELENIUM IN THE DELTA

To evaluate potential linkages between dissolved and particulate selenium from the Delta as modeling inputs, dissolved and particulate selenium concentration data by species and ancillary parameters (TSM, chlorophyll a, salinity) collected from sites in the Delta by Doblin et al. (2006) were examined. The data were collected during low and high flow periods of November 1997 to November 1999. As in Doblin et al. (2006), Delta sites were defined as sites upstream of Chipps Island (38º 02.820N, 121º 53.570W).

The relationships between particulate selenium (µg/g) and different species of dissolved selenium and ancillary parameters were explored. Total particulate selenium concentrations (µg/g) were found to be positively related with selenite, selenate, total dissolved selenium, organic selenide and negatively related with TSM (Figure A.4-1, Table A.4-1). No relationship with chlorophyll a was found if one site with high chlorophyll a concentration was excluded (Figure A.4-2).

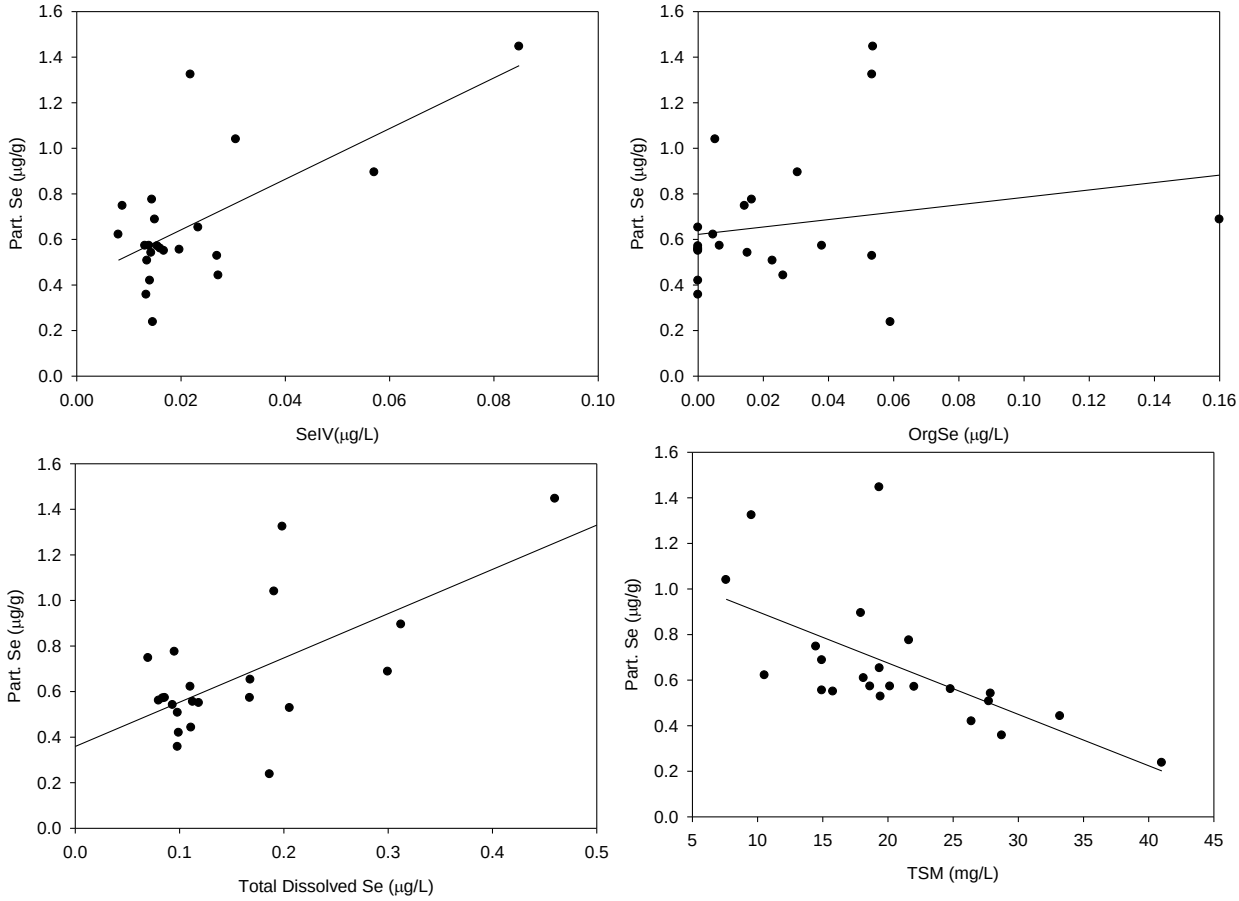

Figure A.4-1 Relationship between particulate selenium and dissolved selenium by species, total dissolved selenium and TSM.

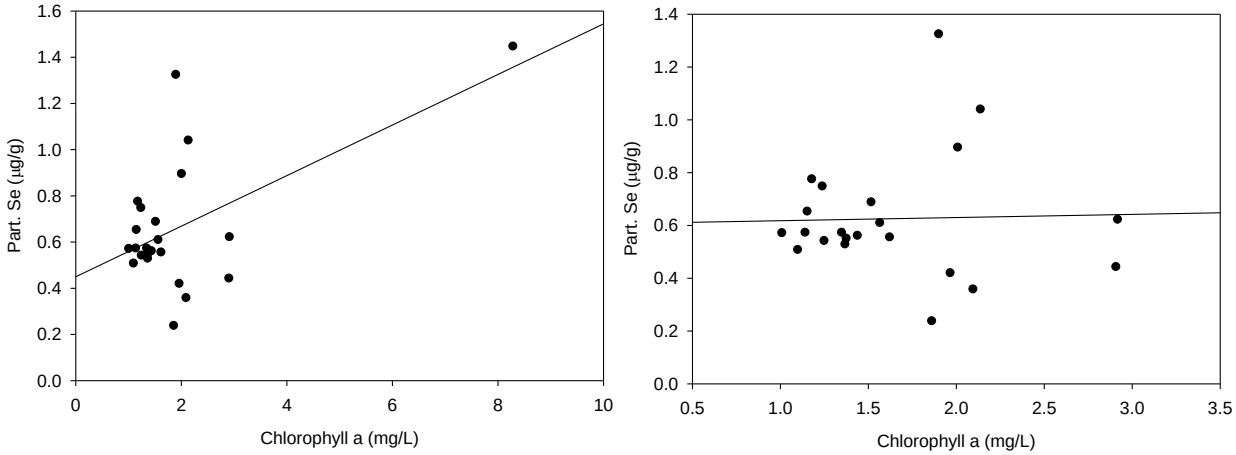

Figure A.4-2 Relationship between particulate selenium concentration and chlorophyll a.

Table A.4-1
Correlation Between Particulate Sselenium and Dissolved Selenium and Ancillary Parameters

Correlation coefficient	Salinity	Se IV	Se VI	Se -II+0	Total Dissolved Se	TSM	Chl a
Total Part. Se (µg/g)	0.05	0.67	0.65	0.20	0.64	-0.62	0.57
PSeivvi (µg/L)	0.02	0.25	-0.18	0.01	-0.10	0.26	0.25
PSe0 (µg/L)	0.12	0.26	0.65	0.13	0.39	-0.24	-0.49
POrgSe (µg/L)	0.18	-0.23	-0.25	-0.07	-0.18	-0.12	0.03

Particulate selenium species in the Delta sites are highly variable, although total particulate selenium shows less variation (Table A.4-2). Particulate organic selenide is highly variable (with CV of 1.006) and is not related to dissolved selenium species or chlorophyll a (Table A.4-2). Particulate elemental selenium shows less variation (CV = 0.674; Table A.4-2) and is positively related to selenate and negatively related to chlorophyll a (Table A.4-2). Particulate adsorbed selenite and selenate show moderate variation (CV = 0.793) and is weakly related to selenite and selenate (Table A.4-2).

Table A.4-2
Particulate Selenium Concentrations by Species and Total Particulate Selenium Concentrations in the Delta (Source: Doblin et al. 2006)

Species	Total Part. Se (µg/L)	Pseivvi (µg/L)	PSe0 (µg/L)	POrgSe (µg/L)
Mean	0.012	0.004	0.006	0.003
Standard Deviation	0.004	0.003	0.004	0.003
CV	0.349	0.793	0.674	1.006
% of Total		31.4	43.6	25.1

The K_d values were species-specific, derived using data collected by Doblin et al (2006) in the Delta. The K_d for particulate adsorbed selenite and selenate (Kd_PSeivvi) was based on ratio between particulate adsorbed selenite and selenate concentration (PSeivvi) and dissolved selenite (SeIV). The K_d for particulate organic selenide (Kd_PorgSe) was based on

ratio of particulate organic selenide (POrgSe) and selenide (Se-II). K_d values for particulate elemental selenium was derived from concentrations of particulate elemental selenium and selenate. The derived K_ds show different degrees of variability. The average K_d values for each species were used in the model (Table A.4-3).

Table A.4-3
Kd values (L/g) used in linking particulate and dissolved selenium in the riverine inputs.

	Average	Low Flow	High Flow
Kd_PSeivvi	15.73	15.89	15.47
Kd_PorgSe	14.23	16.24	9.30
Kd_Pse0	2.65	3.09	2.16

APPENDIX 5: SUMMARY OF THE TECHNICAL REVIEW COMMITTEE PROCESS

TRC REVIEW OF TECHNICAL MEMORANDUM 6: APPLICATION OF ECOS3 FOR SIMULATION OF SELENIUM FATE AND TRANSPORT IN NORTH SAN FRANCISCO BAY

The establishment of a Technical Review Committee (TRC) was identified in the Project Plan for the North San Francisco Bay Selenium TMDL (RWQCB, 2007) to ensure that the scientific basis of the project and, therefore, key decisions and assumptions, are technically sound. The establishment of the TRC also had the goal of providing an efficient process in which highly specialized expert consultation occurs at key steps in the development of the TMDL. The role of the Technical Review Committee was to provide expert reviews of the modeling process as well as credible technical advice on specific technical issues arising from the review process.

Technical Memorandum 6: Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay (TM6) was the third of the TMDL documents to be reviewed by the Technical Review Committee. Previously, the TRC provided comments on *Technical Memorandum 4. Conceptual Model of Selenium in North San Francisco Bay* and *Technical Memorandum 5. Recommendations for Numerical Model Development*.

The purpose of this appendix is to provide a record of the technical review process, present the comments of the Technical Review Committee members, and to identify the actions that were taken in response to the Technical Review Committee's comments on TM6. This summary documents the rigor of a review process that spanned several months. We believe that by capturing the products of this review process an invaluable source of information will be provided for future investigators.

The members of the TRC were:

- Dr. Nicholas S. Fisher, State University of New York, Stony Brook
- Dr. Regina G. Linville, California State Office of Environmental Health Hazard Assessment
- Dr. Samuel N. Luoma, Emeritus, U.S. Geological Survey
- Dr. John J. Oram, San Francisco Estuary Institute

Resumes for the TRC members are presented in Technical Memorandum 8: Recommendations for the Technical Review Committee (Tetra Tech, 2008). The process of selecting the TRC members is also described in the Technical Memorandum 8.

TM6 TRC REVIEW CHRONOLOGY

The following table identifies the steps in the review process and a guide to the sections describing the process:

5A.1. DRAFT TM6 SENT TO TRC FOR REVIEW, MARCH 11, 2009

The Draft TM6 document, directions for the review process, and a request for written comments were sent to the TRC members in advance of a meeting to discuss their findings. The following questions were provided for the reviewer's consideration during the review process:

1. Are the biogeochemical processes associated with selenium captured adequately in the model formulation? Is there an opportunity for simplifying the formulation further, or is there a need to incorporate additional processes?

2. Is the biological uptake adequately described? Are there better ways of defining the uptake into predator species of interest?

3. Has the model been calibrated and evaluated appropriately? Have all available datasets been utilized? Do you think the level of fits achieved, including poor fits in some instances, are nonetheless adequate for the use of this model in the selenium TMDL?

4. Do the scenarios tested provide enough insight into the model performance? Do you feel a need to consider additional loading scenarios in the modeling report that would enhance understanding of the model performance?

5. Are the strengths and weaknesses of the modeling approach and results clearly laid out?

6. Are there any concerns with the use of this modeling framework in the development of the selenium TMDL in North San Francisco Bay?

A5.2. TRC REVIEW MEETING HELD ON APRIL 8, 2009

A one-day meeting was held with the goal to evaluate the "formulation, calibration, and performance of the modeling tools developed to assess transformation in the North Bay ecosystem in response to changing selenium loads". The meeting consisted of presentations by Tetra Tech, a discussion of the key comments received from TRC members, and a preliminary report to the Regional Water Quality Control Board, San Francisco Bay Region (Water Board) on the findings of the TRC. In addition to the TRC members the attendees included representatives of the TMDL Advisory Committee. The following is a complete list of attendees:

Technical Review Committee Members

Regina Linville, CA State Office of Environmental Health Hazard Assessment
Nicholas Fisher, State University of New York, Stony Brook
John Oram, San Francisco Estuary Institute
Sam Luoma, US Geological Survey

Advisory Committee Representatives

Michael C. S. Eacock (Chris), Bureau of Reclamation, South-Central California Office
Eugenia McNaughton, EPA
Diane Fleck, EPA
Bill Beckon, US Fish and Wildlife Service
Al Middleton, Valero Refinery
Dennis Bolt, Western States Petroleum Association
Timothy Stevens, Department of Fish and Game
Theresa Presser, US Geological Survey
Rosalind Becker, Baykeeper

Regional Water Quality Control Board

Barbara Baginska, Selenium TMDL Project Manager
Naomi Feger, TMDL-Planning Section Lead

Tetra Tech

Tom Grieb, Project Manager
Sujoy Roy, Lead Author - Technical Memorandum 6
Limin Chen, Co-Author and Modeler - Technical Memorandum 6

At the conclusion of the meeting there were three main messages from the TRC. First, the TRC agreed that the model is a legitimate tool to use in building the TMDL, second there is a need to test and to demonstrate the robustness of the model, i.e., to describe how the model is working and to identify the inherent constraints. Third, there needs to be more transparency on how the model works, and the report needs to do a better job of communicating the model results to the stakeholder community.

The results of the TRC review and meeting discussion items are presented below in two parts: (1) a summary of the meeting discussions, and (2) the complete set of TRC comments received and the responses to these comments.

Summary of April 8, 2009 Meeting Discussions

Written and verbal comments from the TRC can be grouped into six primary categories. The following is a summary of specific comments in these six categories and the proposed follow up actions:

Unclear Description of Key Steps in the Modeling Process and of Modeling Assumptions

Here are some of the items/issues identified:

- *How are dissolved Se loads at Vernalis converted to Se concentrations in Bay? (see Section 3.3, p. A.5-16, S. Luoma, Comment 1)*
- *What is the fate of organic Se (biotic) entering the modeled system from the SJR and how is that source incorporated into the model?*
- *An explanation for the "tripling the load" of particulate material scenario is essential. (see Section 3.3, p. A.5-18, S. Luoma, Comment 4)*
- *The slide title "Selenium Loads to Meet Hypothetical Target of 7ug/g Target" (also referred to as the "Green Bar Graph" needs to be better explained. (see Section 3.3, p. A.5-19, S. Luoma, Comment 9)*

Tetra Tech Response: We will focus on explaining better the Delta boundary condition, and the linkage between loads at Vernalis and Freeport, to loads entering the Bay, including particular selenium species that originate in the San Joaquin watershed (e.g., organic and particulate selenide). Similarly, we will add more explanation of the linkage between the dissolved and particulate riverine concentrations at the Delta boundary.

There will be added discussion of the basis of the scenarios, and the scenarios evaluated will be modified to a wider range of particulate loads at the Delta boundary.

An explanation will be added to TM-6 to clarify whether input parameters used represented concentrations or loads and to explain how loads were computed at certain modeling steps.

The section evaluating the impact of various load reductions of a bivalve target of 7 ug/g in the report (Section 5.2), will be revised to explain the approach where loads categories were removed one by one, and to explain the conditions that defined the exceedance of the 7 ug/g target. Graphical presentation of the results will be also revised.

Robustness of the Final Conclusions. The effects of initial conditions and embedded modeling decisions are not clearly described, and it was not clear to the TRC that the effects of the initial conditions were adequately tested.

- "It is very important for the regulatory analyses that different scenarios explicitly *consider* different particulate Se concentrations at the head of the estuary" (S. Luoma, Comment 2)
- "The concentrations of particulate organo-Se should be viewed as

potentially quite variable. That variability should be considered in scenarios concerning influences of changing loads and perhaps in the base calculations. (S. Luoma, Comment 3)

- "But the assumptions, explanation and interpretation of the model results are insufficient for even experts to fully understand". (S. Luoma, Comment 7)

- The need to better understand the effects of seasonality and wet/dry-year conditions on the modeling results was identified in meeting discussions.

Tetra Tech Response: We will consider a wider range of particulate concentrations at the riverine boundary of the estuary, and will present these results in TM-6.

The role of organo-Se will be discussed through example calculations demonstrating the effect of higher or lower values at a key location (ranging, for example from one-third to three times the model estimated value).

We understand the TRC's perspective on the need for more transparency. We will add more explanation and/or graphical interpretation at key places in the report, especially on topics relating to the boundary conditions and scenarios, which were the source of many questions at the TRC meeting.

The scenario sections will be modified to include presentations of loading and response values at both annual and seasonal scales.

The uncertainties associated with the model results are not adequately described.

- Express predictions in terms of uncertainties (see Section 3.3, p. A.5-18, S. Luoma, Comment 7). Sam also noted that the report did a good job of listing know/unknowns. We should try to build on this existing description to facilitate a broader understanding of uncertainties.

- In the concluding remarks by the TRC, requests were made to identify uncertainties as well as research and monitoring needs. Identifying these needs from the modeling perspective would make a distinct contribution.

Tetra Tech Response: The revision to TM-6 will carefully consider the role of uncertainty on the major recommendations of the report, and whether these might be influenced by the uncertainty in current understanding of the processes. The development of research and monitoring needs will be a focus of the TMDL development.

The overall conceptual model, captured by ECoS3, is not adequately described.

- One *of* the consensus items, identified above, was the need to describe how the model is working and to identify the inherent constraints. The TRC suggested that we present a simple box diagram that represents the steps or elements in the model and that provides an explanation of the key equations and the consequences of their inclusion.

Tetra Tech Response: As recommended by the TRC, to aid understanding of model conceptualization, Tetra Tech will include a section representing the

calculations embedded in ECoS at a key location (e.g., near Rio Vista or in Carquinez Strait) with numeric values of the different pools and fluxes, so that the interested reader can better understand the model processes.

The rationale for the selection of model scenarios is not adequately described/defended.

- The report should explain why these scenarios were selected and what the results show in terms of the required regulatory decision-making process.

Tetra Tech Response: The scenarios presented were intended not as specific endpoints for use in the TMDL, but to demonstrate the response of the model to specific inputs. However, given the discussion at the TRC meeting, we propose to present a wider range of boundary conditions and scenarios to meet this objective, and as discussed above, more explanation on what these mean in the real world. The revised model will be used to test specific load-alternation scenarios that the Regional Board may consider in its planning for the TMDL and these results will be presented in a follow-up technical memorandum.

The communication of risks associated with the ecological endpoints is not adequately addressed.

- There were several comments on the characterization of risk and characterization of assumptions, e.g., food sources, as worst case.

- TM-6 needs to explain how the ECoS3 modeling results are used in the assessment of risk to fish and bird receptors. TM-6 could also expand the discussion of ECoS3 modeling results on the ability to meet alternative TMDL numeric endpoints.

Tetra Tech Response: We will review the discussion of risk and risk assessment terminology and address these concerns. The model runs will be updated with inclusion of predictions of concentrations in higher trophic levels that are the preferred target for the selenium TMDL.

A5.3. RESPONSE TO COMMENTS AND REVISED TM6 DISTRIBUTED, JUNE 19, 2009

The written comments received in response to the March 11, 2009 review request (see Item 1 above) were addressed by Tetra Tech and forwarded to the TRC members along with the Revised Draft TM6. The following is the record of comments submitted by the TRC and responses to those comments:

A5.3.1 Review of Technical Memorandum 6 by Nicholas Fisher, March 2009

Tetra Tech responses have been inserted following the reviewer's comments with this exact font and color.

Reviewer's Comment 1: *Overall, this document (Technical Memorandum 6) reads like a modeling exercise put together by a team of modelers and environmental engineers rather than by biological and chemical oceanographers. The authors have done a generally fine job in mining the available literature and trying to make sense of it, and I found the document fairly well-written and interesting. As I elaborate below, there are some key details that seem to be skirted over and yet these details may play important roles in the outcome of the model predictions. Most of the details regard information about phytoplankton and Se levels in suspended particles, including species compositional shifts in phytoplankton communities – this may be key, since there are enormous differences among algal species in their ability to take up Se from ambient water – and problems in using Se levels in total particulate matter rather than the phytoplankton, which is what many of the herbivores eat. I believe that the authors recognize that the bioconcentration of Se in particulate matter is key to understanding the subsequent Se loadings in the food web–not the only key, but very important–and in particular it is essential to understand the bioaccumulation of Se in living phytoplankton. This is because it is the phytoplankton, with much variation among species, that concentrate Se appreciably out of the ambient water and convert it rapidly to organic selenides. The organic selenides are the form of Se that is assimilated very appreciably by the herbivores, and it is noteworthy that many herbivores are often quite selective in their feeding on phytoplankton (as opposed to all suspended particles). I also propose a possible straightforward solution – a solution which would need to be tested in the field – to addressing this uncertainty without investing heavily in examining the species compositional changes over space and time in phytoplankton communities.*

Tetra Tech Response: We are in full agreement with the reviewer's comment regarding the role of phytoplankton in controlling selenium bioaccumulation. In response, we have made numerous changes in TM-6, including descriptions of selenium uptake as determined in published laboratory studies, an analysis of selenium uptake by consideration of different phytoplankton species, and consideration of a wide range of uptake rates (up to a hundred times greater than the rate used for the base case). Analysis using selenium:carbon ratios that have been determined for different species, shows that the values that are consistent with observations in the bay are in the high range of laboratory measurements (15-30 □g/g Se:C). Values that are much lower than this range result in calculated particulate selenium concentrations that are significantly lower than observed values (Section 4.7).

Reviewer's Comment 2: *Below I list comments on the document in the order in which these issues appear in the document. I have put an asterisk next to those issues that I consider to be most significant.*

Page 1-8 (4th bullet), as I noted previously, it is inappropriate to use Kd values for Se, at least for Se taken up by phytoplankton. This is because Se uptake is an energy-requiring process–the Se is not in equilibrium between particle surfaces and the dissolved phase (there is no appreciable passive uptake of Se by

phytoplankton: Fisher & Wente 1993), and because once Se is taken up by cells it is rapidly converted to organic selenides (mostly selenoamino acids), and so the organic selenides inside the cells are clearly not the same species of Se as the inorganic selenite that was taken up by the cells and they are therefore not in equilibrium. I noted that problems with using Kd values was noted by the authors later in the document.

Tetra Tech Response: The uptake of Se is modeled using first order rate constants. The Kd values were used for comparison with other studies.

Reviewer's Comment 3: *Page 2-8, top paragraph: "Data on microbial uptake of Se was not available in the bay." This is not correct–see Baines et al. (2004).*

Tetra Tech Response: The uptake rates measured in Baines et al. (2004) were for the Delta water only. Phytoplankton and microbial communities in the Delta may be very different from that in the Bay (due to marine water influence).

Reviewer's Comment 4: *Page 2-9, Table 2-1: Why are Riedel selenite uptake rates 10 times higher than those of Baines et al. (2004). Is this attributable to the fact that Riedel used algal cultures, whereas Baines used natural phytoplankton assemblages, consisting almost surely of some non-living material?*

Tetra Tech Response: The rates reported in the original papers are absolute rates, not rate constants normalized to ambient selenite concentration. The difference in rates is due to several reasons:

a. Different sources of phytoplankton species used in the culture

b. Different ambient selenite concentrations used in the culture (10 ug/L vs. 0.3 ug/L).

c. Different chlorophyll concentrations used in the experiment.

When normalized to ambient selenite concentration, the rates of uptake are higher from Baines et al. (2004).

In the revised TM-6, rates are reported in consistent units, normalized to chlorophyll a and selenite concentrations.

Reviewer's Comment 5: *Page 2-12, Table 2-2: incomplete, many species not shown.*

Tetra Tech Response: The species shown are for the 0.15nM experiment (Table 3 and 5 in Baines and Fisher, 2001).

Reviewer's Comment 6: *Page 2-13: I do not understand Eq. 31–how was that arrived at?*

Tetra Tech Response: The equation assumes sine wave concentration of selenium concentrations. The concentration varies from a mean concentration with certain period/frequency. It is the equation originally used in Meseck (2002) and does not imply mechanistic significance; it is primarily a fitting function.

Reviewer's Comment 7: **Page 3-2, Table 3-2: Why use Riedel et al's selenite and organic selenide uptake rates by phytoplankton instead of Baines'? Note that Riedel's study was with freshwater phytoplankton.*

Tetra Tech Response: From a calibration standpoint, the reason for using Riedel's rates is that they gave results consistent with observations in the bay. The

uptake rate is an important link between dissolved and particulate concentrations. In the revision to TM-6, we consider a range of values of uptake rate (reaching values up to 100 times higher than Riedel's rates) to evaluate the impact on overall calibration. This analysis (Section 4.3) found that increases in uptake rate must be matched by increases in calibrated mineralization rate, failing which both dissolved concentrations and Se:C ratios are significantly different from observed values. This analysis provides support for a general range of uptake rates that are applicable for the bay, and indicates that the uptake rate to mineralization rate ratio needs to be approximately constant for other variables to remain consistent with observed values.

Reviewer's Comment 8: **Page 3-7: Riedel uptake rates were higher, not lower (see Table 3-2) than Baines' rates. Also, Riedel used freshwater algae–how applicable is this for North San Francisco Bay? Also, it is important to keep in mind that Se:C ratios in the field are for seston, much of which is NOT phytopankton. Dead organic aggregates will have high C concentrations but will not be effective in taking Se up out of ambient water. Se:C ratios in living algae should be much greater than that in seston, and it's often the phytoplankton that are ingested by herbivores (not total seston), so it is important to know the phytoplankton Se concentrations (not just seston). I realize this is a tricky business, but it is possible to determine this with current technology (for example, using x-ray fluorescence microscopy with a synchrotron), although this is very specialized, somewhat expensive, and time-consuming (see Twining et al. 2003). It does provide definitive and unambiguous answers, however. As well it is dependent upon getting sufficient "beam time" on the appropriate synchrotron (such as at the Advanced Photon Source at Argonne National Laboratory); nevertheless, it is do-able. Currently though it is clear that the available data base on phytoplankton Se loads is lacking, and models to understand and predict impacts of Se biogeochemistry in San Francisco Bay will be necessarily limited as a consequence.*

Tetra Tech Response: Based on the responses above, when normalized for selenite and chlorophyll a concentrations, the Baines et al. (2004) rates are higher than the Riedel et al (1996) rates (Table 2-1 in TM-6). The key test for the use of these rates in this work is whether they can be used to explain the particulate and the dissolved concentrations. If the uptake rates are too high, the particulate concentrations, and the Se:C ratios will be exceeded, and the dissolved concentrations will be too low. Likewise, if the uptake rates are too low, the dissolved concentrations will be exceeded and the particulate concentrations will be too low. Another control on the particulate and dissolved concentrations is the mineralization rate of selenium that has been taken up byplankton, i.e., the rate at which particulate organic selenide is converted to dissolved selenite. For the simulated values to remain consistent with observations, the best fit uptake/mineralization rates ratios are similar. The main point of this exercise is that the calibration can be used to bound the range of uptake rates and mineralization rates, and that these are in the range of values reported from controlled laboratory studies.

Additional analysis with the model also provides ranges of plankton Se:C ratios that are consistent with particulate selenium data (all species). A test of these ratios with direct synchrotron measurements of Se:C ratios in live algal cells from the bay would be an intriguing comparison.

Reviewer's Comment 9: So, a thought: organic selenides in particulates are key (that is what is assimilated so efficiently from phytoplankton into herbivores) and

they probably represent mostly phytoplankton Se. The other forms of Se (inorganic and elemental) are probably sorbed to non-living material and won't be an important Se source for animals. By knowing the particulate organic selenide load, it is possible to evaluate most of the Se that is likely to be bioavailable for the animals in phytoplankton, regardless of their taxonomy. Using this approach for the purpose of modeling, we may not need to know the phytoplankton species composition and track its changes spatially and temporally (tedious work, and very time-consuming). The particulate organic selenide load will almost certainly be associated primarily with intact phytoplankton (potential food for the herbivores). Not only is there a problem in looking at seston vs. phytoplankton for understanding Se but there is also a problem with the non-specificity of using chlorophyll a as a measure of phytoplanktonic Se. That is because all taxonomic groups of algae have chlorophyll a–thus this pigment is a pretty good indicator of total algal biomass. However, we know from Baines and Fisher's (2001) paper (cited in this document) that there are very large differences (up to 4-5 orders of magnitude) among different phytoplankton types. Chlorophytes (green algae), in particular, display much lower Se concentrations than most diatoms, dinoflagellates, coccolithophores, and other algal groups. Thus, relating Se accumulation with chlorophyll a can be very misleading, depending on the algal species that happen to be dominating a particular body of water at a particular time. Bear in mind that phytoplankton species composition (not just biomass) in many bodies of water changes substantially with season, and so the bioavailable organic selenides could also change seasonally, depending on the composition of the algal communities being considered. Therefore, a key missing piece of information in this document (at least, I didn't see it) is the species composition of the algal community in different regions and seasons. This may well be known (Lehman's work, perhaps? Cloern's?) and should be factored in to the models if species composition data are available. Or, as noted above, you could consider relying on the organic selenide load associated with total suspended particulate matter.

Tetra Tech Response: The current data in the bay can be used to infer temporal distributions of phytoplankton species or groups, such as diatoms, chlorophytes, cyanophytes, and flagellate algae (Lehman, 2000). The dominant species of phytoplankton vary across space and time. The general finding is that diatoms, green, bluegreen and chrysophyte are more abundant during wet and normal years. While during dry years, cryptophytes, green flagellates, and miscellaneous flagellates are more abundant. Selenium concentrations in phytoplankton generally follow the order of: golden brown algae> dinoflagellates > diatoms > green algae. The increase of golden brown algae and green algae in recent years may have different effects on particulate selenium concentrations associated with phytoplankton. However seleniumconcentrations in flagellates have not been measured. When data from 1999 are evaluated, the particulate selenium data provide a strong basis for allowable value of Se:C ratios, typically 15 □g/g or greater. Values at the low end of the Se:C ratio spectrum result in particulate selenium lower that observed. The modeling exercise provides a means to evaluate the laboratory results, and suggest further experimentation, especially when Se:C ratios have been determined for specific concentrations only, and are known to vary with concentration.

The suggestion for measuring particulate organic selenide directly as a surrogate for species of direct relevance to clam uptake is a good one. However, we are

strongly in favor of more selenium species data in the bay in general, and would even support the measurement of particulate selenium (all species) as a starting point (addressed in Section 6.7).

We are aware of the difference in Se:C ratios in seston and phytoplankton. The model simulates Se:C ratios in phytoplankton only and were compared to measured Se:C in phytoplankton for a few species that are present in the Bay (Cryptomonas sp. – golden brown algae; Prorocentrum minimum- dinoflagellates).

Reviewer's Comment 10: Page 3-38: I'm curious–why did the riverine Se loadings drop 2-5 fold after 1998?

Tetra Tech Response: This is largely due to change in flows.

Reviewer's Comment 11: Page 3-56: Poor fits for particulate organic selenides–attributable to different algal species (see above)?

Tetra Tech Response: We are unable to explain the poor fits, not the large variation in organic selenides in the bay at stations in close proximity to one another. This may be a result of local-scale processes that are not captured in the model, including local-scale algal species variation, or may be a esult of the analytical technique used to determine particulate organic selenide (by difference from adsorbed selenate+selenite and elemental selenium).

Reviewer's Comment 12: **Page 4-8: Need for characterization of phytoplankton types–should do simulations for different types of phytoplankton, not just varying chlorophyll a.*

Tetra Tech Response: We have performed this in Section 4.7.

Reviewer's Comment 13: Page 5-7: Stewart & Luoma (2008) not in reference section.

Tetra Tech Response: There is an error in the reference. Should be Stewart and Luoma not M.Jagger.

Reviewer's Comment 14: Page 5-11 to 5-14: I found it hard to follow the argument being presented on these pages.

Tetra Tech Response: This section has been revised extensively.

Reviewer's Comment 15: Page 5-14 to 5-15: As noted earlier, can't use Kds; meaningless to use Kds for organic selenides where particulate Se form is organic and ambient dissolved Se is inorganic.

Tetra Tech Response: This section has been deleted.

Reviewer's Comment 16: *An important question: What is the fate of the phytoplankton entering the Bay-Delta system from rivers, especially once they hit saline waters? Presumably these cells are enriched in organic selenides, where the Se was originally obtained from the rivers, but once they reach saline waters, do they rapidly die and is the Se associated with them remineralized? I assume that *Corbula amurensis* is eating estuarine/marine phytoplankton species, not the freshwater cells that may have washed into the system from the rivers.

Tetra Tech Response: In the model, phytoplankton are treated as a single constituent through chlorophyll a. When riverine phytoplankton enter the bay, the selenium initially remains in the organic particulate compartment, and is mineralized over time. Selenium is also added to the algal compartment through

uptake. Phytoplankton growth and decay, in aggregate, is tracked in the model, as is phytoplankton-associated selenium. However, for the purpose of the calculation, the algae are treated as a single species.

Reviewer's Comment 17: *Another question: if the levels of Se loading that need to be reduced are deemed unrealistic, does this mean that Se levels in San Francisco Bay were always dangerous to diving ducks and sturgeon and other fish that ate benthic bivalves, or has the story hinged primarily on the introduction of *Corbula amurensis*, which tends to bioconcentrate Se to higher levels than other bivalve species? If the latter, then more research on the biology of *C. amurensis* may be as useful as investing heavily in reducing Se loadings via the rivers, with the hope that some strategies may develop to reduce their populations and thus reduce the conduit of organic selenides to wildlife and fish. This is not meant to support the idea that we should do nothing about Se loadings–in fact we should do everything possible to reduce them–but a parallel effort, if it is feasible and will do less harm than good, to reduce the populations of this invader species may also be money well spent.

Tetra Tech Response: Based on available information, the high bioaccumulation in Corbula amurensis is an important cause of high levels in predator species. The control of invasive species along with possible load modifications is an alternative that the Regional Board may choose to address during the implementation phase of the TMDL. Note that the other common clam species present in the bay and Delta, more on the freshwater side, Corbicula fluminea, is also an invasive species throughout much of the United States.

References cited not already in document:

Fisher, N.S., and M. Wente. 1993. The release of trace elements by dying marine phytoplankton. Deep-Sea Research 40: 671-694.

Twining, B.S., S.B. Baines, N.S. Fisher, J. Maser, S. Vogt, C. Jacobsen, A. Tovar-Sanchez, and S.A. Sañudo-Wilhelmy. 2003. Quantifying trace elements in individual aquatic protist cells with a synchrotron x-ray fluorescence microprobe. Analytical Chemistry 75: 3806-3816.

A5.3.2 Review of Technical Memorandum 6 by Regina Linville, April 6, 2009

Tetra Tech responses have been inserted following the reviewer's comments with this highlighting.

Reviewer's Comment 1: *The following is provided as a preliminary review of the major issues. The discussions during our upcoming meeting should clarify several issues and raise additional questions. This report reflects the large amount of work performed by the authors and previous modelers on the loading, fate and transport, and bioavailability of selenium in northern San Francisco Bay. The authors have provided a good description of the major factors involved in these processes. Similarly, a thorough analysis of the modeling framework is provided.*

I have outlined my concerns below and look forward to discussing these with the authors and review committee.

A5.3.2.1 The critical role of phytoplankton

The report contains a good description of the importance of phytoplankton in the overall bioavailability of selenium. It appears that the model does not provide a mechanism to distinguish the relative importance of "particulate organic selenide" as phytoplankton compared to suspended sediment (importance to bivalve accumulation). Is that true?

Tetra Tech Response: Phytoplankton associated particulate organic selenide has the same assimilation efficiency with other forms of particulate organic selenide. The assimilation efficiency of these forms of selenium is different from that associated with inorganic forms (adsorbed selenate and selenite and elemental selenium). The role of particulate selenium speciation in clam uptake is clarified further in Section 2.7.

Reviewer's Comment 2: *Section 4.3 addresses part of this question, but it would be helpful to extend that analysis to the influence on predicted bivalve and predator bioaccumulation. Similarly, the loading that most impacts the phytoplankton fraction of particulate organic selenide if of high interest.*

Tetra Tech Response: Modeled values in bivalves and predator species are shown in Section 3.4. The scenario analysis in Section 5.1 includes now includes analysis of impacts to bivalves for all cases considered.

Reviewer's Comment 3: *I would like to further discuss the treatment of phytoplankton and particulate material in the model.*

Tetra Tech Response: The analysis of phytoplankton species as well as uptake rates has been expanded in Sections 4.3 and 4.7.

A5.3.2.2 Model framework and risk assessment

Reviewer's Comment 4: *The bird toxicity reference values (TRVs) and hazard quotients (HQs) in birds are referred to as highly conservative. I disagree. How are these TRVs conservative? In the study used for the TRV (Heinz et al., 1989) the LOAEL (~ 0.7 mg/Kg-day) resulted in malformations in 7% of unhatched eggs compared with < 1% in controls (NOAEL is ~ 0.3 mg/Kg-day). The next dose level (~ 1.4 mg/Kg-day) resulted in malformations in 68% of unhatched eggs. These values are very close together, which is consistent of our knowledge of selenium toxicity in general (i.e., narrow range between nutritional and toxic values). Additionally, the assumption that 100% of diving duck's diet consists of clams is not particularly conservative. The authors statement that "**. . . there are a large number of conservative assumptions that are incorporated in the estimated HQs. Therefore, HQs that are in the single digits (i.e., <10) are often not considered to represent significant risks." is not supported (nor is it a general assumption in ecological risk assessment). For example, a HQ of 2 based on the NOAEL TRV corresponds to a dose that is equal to the observed LOAEL (and 7% of eggs with malformations). A HQ of 2 based on the LOAEL TRV corresponds to a dose that resulted in malformations in 68% of unhatched eggs.*

Tetra Tech Response: The language has been modified to: "An HQ less than 1 indicates that there is a negligible potential for adverse ecological impacts due to exposure to a particular COPEC, whereas an HQ greater than 1 indicates that there is a potential for adverse ecological impacts due to exposure to that COPEC.

However, there are a large number of conservative assumptions that are incorporated in the estimated HQs and a value slightly greater than 1 does not indicate significant risk. ”

Reviewer's Comment 5: *The development of the TRV was not described in this document or in TM-3. (However, these TRVs are very similar than those developed by EPA Region 9's Biological Technical Assistance Group (BTAG), which are used by DTSC. See:*

http://www.dtsc.ca.gov/AssessingRisk/upload/Eco_Btag-mammal-bird-TRV-table.pdf).

I suggest either providing a detailed justification of the TRV development, or using the BTAG numbers.

Tetra Tech Response: The text has been modified to clearly define the TRVs used in the work. This exposure study used in this calculation is the same as that used by BTAG (Heinz et al., 1989).

Reviewer's Comment 6: *More information is needed regarding the Trophic Transfer Factors.*

Tetra Tech Response: General guidance on the TTFs used in this work was provided by Sam Luoma and Theresa Presser, based on a review they are developing. A more complete citation will be presented when available.

Reviewer's Comment 7: *The authors refer to the exposure scenario as a* ***worst case scenario*** *since it is based on the accumulation by, and consumption of, Corbula amurensis. This seems to suggest that the predicted exposure would only happen under extreme ('the worst') circumstances. Corbula is the main species of bivalve in the study area and a dominant prey item of diving ducks and sturgeon. A more clear description would be that the modeled scenario applies specifically to top predators of the benthic food web.*

Tetra Tech Response: The terminology worst case scenario is no longer used in the report. Language similar to that suggested here is used in Section 7 to summarize the results of this aspect of the analysis. The following language is used: “The bioaccumulation analysis presents a focused and possibly incomplete evaluation of the adverse effects of selenium uptake on fish and bird species that are benthic feeders. The bivalves chosen for examination in this work, Corbula amurensis, are very efficient at bioaccumulating selenium, more so than other bivalve species. In the bioaccumulation analysis, it is assumed that the predator species, white sturgeon and diving ducks, feed exclusively on this bivalve species. Additionally, the prediction of tissue concentrations in white sturgeon and diving ducks does not take into account the observed seasonal differences in bivalve selenium concentrations. The current assessment of risk to predator species in the bay from selenium uptake is largely a result of the presence of Corbula amurensis, despite the two-decade long efforts to control non-point sources in the Central Valley and point sources in the bay.”.

Reviewer's Comment 8: *I would like to discuss these issues further and their implications in the model framework.*

A5.3.2.3 Model calibration and evaluation

Reviewer's Comment 9: *I have several questions regarding the calibration and evaluation section that I suspect will be clarified during our meeting. The questions involve the choice of parameters, specific calculations, and calibration details.*

A major concern in this section is the lack of comparisons between observed and predicted values in top predators. My concern regarding the discussion of risk is described above.

Tetra Tech Response: Model predicted selenium concentration in predators are compared with available data in Section 3.4.

A5.3.2.4 Model predictions and proposed uses

Reviewer's Comment 10: I have several questions regarding model predictions and proposed uses that will likely be answered during Tetra Tech's presentation on Wednesday.

I would like to discuss some of the general conclusions in light of the sensitivities identified in the report. An example is the prediction that particulate selenium will not respond to a decrease in selenium loading. The authors highlight the implications of this prediction in the executive summary and elsewhere. However, it appears that prediction of selenium in phytoplankton is one of the weaker functions of this model. Is the emphasis justified considering the known limitations of this model?

Tetra Tech Response: The role of phytoplankton uptake in the model is evaluated in much more detail in the revised TM-6, Section 4, providing more support for the general conclusion.

A5.3.3 Review of Technical Memorandum 6 by Samuel N. Luoma, Emeritus, U. S. Geological Survey, April 13, 2009

Tetra Tech responses have been inserted following the reviewer's comments with this exact font and color.

Reviewer's Comment 1: *Model description is unclear about how dissolved Se loads at Vernalis are converted to Se concentrations in Bay. A factor is inserted for Delta removal. Is this tied to some physical process? Is it a constant? What is the value of the removal "constant"?*

Tetra Tech Response: Figure 2-16, Concentrations and flows used to compute loads of selenium, dissolved and particulate, and by species, for the Sacramento and San Joaquin Rivers, has been added to TM-6. This figure includes a summary of the methods used to calculate the dissolved concentrations and loads to the North Bay (confluence) based on 1999 speciation data from Vernalis. For the San Joaquin River, the dissolved concentrations at the confluence were calculated by multiplying the dissolved selenium concentrations at Vernalis by an input constant (1 – removal constant). Separate input constants, presented in Table 3-3, were used for the three species in the dissolved phase: SeIV (0.326), SeVI (0.26), SeII (0.534). The loads at the confluence were calculated by multiplying the "new" dissolved concentrations by the flow (difference between the Net Delta Outflow Index and flow from the Sacramento River at Rio Vista) at the confluence. Dissolved concentrations in the Bay are then determined by the advection, dispersion and transformation equations described in Section 2.

Reviewer's Comment 2: *As we discussed repeatedly, it is very important for the regulatory analyses that different scenarios explicitly consider different particulate Se concentrations at the head of the estuary. As it stands, every analysis of effects of changing Se load in the rivers only considers the effect of that load on the slope in Fig. 3-43. Unless the river boundary condition is explicitly changed, the y-intercept will always stay the same in plots like 3-43. i.e. Several riverine-boundary-condition-particulate-Se-concentrations should be considered with each scenario wherein effects of changing loads in the river are considered. The final conclusions cannot be robust until this factor is better taken into account.*

Tetra Tech Response: Section 4-4, Varying seawater and riverine boundary particulate selenium concentrations, was added to TM-6. The effects of higher and lower bounds of riverine concentrations for different selenium species were investigated. The sensitivity analyses conducted include the evaluation of the effects of different endmemeber particulate concentrations on simulated particulate selenium concentrations (Figure 4-15) and selenium concentrations in bivalves (Figure 4-16).

Reviewer's Comment 3A: *It is a little worrisome for the TMDL that the model cannot explain the high variability in ug/g Se in particulates, in particular in particulate organo-Se. The concentrations of particulate organo-Se should be viewed as potentially quite variable. That variability should be considered in scenarios concerning influences of changing loads and perhaps in the base calculations. For example, it appears that 0.468 ug/g was chosen as the Se concentration for PSP. This is at the lowest end of the range of concentration that Doblin et al observed at the upstream end of their sampling. What would happen to the final conclusion (reducing loads make little difference) if you started with a PSP-Se of 0.8 or the maximum of 1.5 ug/g. If you start at a higher riverine endmember isn't easier to have an impact if you reduce loads from the river.*

Tetra Tech Response: Lower and higher boundary conditions for riverine and seawater endmember concentrations were simulated. The results of varying the endmember concentrations on model simulated particulate selenium concentrations are presented in Section 4. The effects of changes to the endmember concentrations on the comparisons of base case results with reduction in point-source loads are presented in Section 5.

Reviewer's Comment 3B: *Need to adjust marine endmember. Just as the riverine endmember is probably too low, the marine endmember is probably too high. The open ocean, where these data (Cutter and Bruland, 1984) are from is completely phytoplankton and their detritus (no inorganic component). The coastal zone is likely to have lower Se concentrations. Why not use a mean of the Doblin observed values at the seaward-most site, along with and higher riverine boundary condition to directly test the effect of reducing loads? The important problem here is that one cannot differentiate the effect of internal productivity changes vs the ocean endmember in determining the positive slope for the particulate (ug/g) with salinity.*

Tetra Tech Response: The original calibration of the model resulted in the selection of a seawater boundary value of 1.22 ug/g for particulate selenium. In Section 4.4.1 the model simulations are re-run using a particulate selenium concentrations measured at the Golden Gate by Doblin et al (2006) as the endmember concentration for particulate selenium (~0.9 ug/g). Simulated

selenium particulate selenium concentrations in the water column and selenium concentrations in bivalves show some differences from the original simulations. The results are presented in Figures 4-12 through 4-14.

Reviewer's Comment 4: *It is essential that the scenario of "tripling the load" of particulate material be explained. What was done here. What was tripled. What was the TSM condition? What is the mix of particulate species. Why is the intercept only doubled when the concentration is tripled? I would like to see a table that shows the steady state uptake from each type of particulate Se; perhaps it would be easier then to see. I think we understood this by the end of the day, but other readers will not understand it.*

Tetra Tech Response: Table 5-1 was prepared to more fully describe the loading factors used for each of the scenarios. In Scenario 7, for example, the riverine particulate selenium loads consisting of BEPS, PSP and Phytoplankton were increased by a factor of three.

Reviewer's Comment 5: *What happens when nutrients inputs increase, as they might if SJR inflows rise?*

Tetra Tech Response: We did not change the concentration of nutrients in these scenario model runs. A large effort would be required to adequately address the nutrient question, and the focus of this report is the examination of the ability of this model to address the behavior of selenium in the North Bay. A series of specific questions regarding the interaction of increased nutrient concentrations and selenium loading

scenarios could be addressed in subsequent analyses that are planned as part of the TMDL effort.

Reviewer's Comment 6: *Is the model useful? Decent job; very useful effort with state of science. The problem is not in the model; it is legitimate. But the assumptions, explanation and interpretation of the model results are insufficient for even experts to fully understand. The base cases also need to be rerun with different boundary conditions, as suggested above. How important are those boundary conditions to the final conclusions?*

Tetra Tech Response: Sections 4 and 5 have been revised to address these questions regarding the effects of changing boundary conditions, and the descriptions of the results have been enhanced to provide support for the conclusions presented in Section 6.

Reviewer's Comment 7: *Express predictions in terms of uncertainties. Values range from this to this under condition 1 and condition 2 (reasonable for system). Identify where we need data to reduce uncertainty.*

Tetra Tech Response: The presentation of the results in Section 5 (e.g., Figures 5-3 – 5-5) was revised to show the range of effects from modifying the magnitude of the loads from the various sources. In Section 7, recommendations are made for additional efforts to reduce uncertainties and increase the understanding of the factors that affect selenium biogeochemistry in the Bay.

Reviewer's Comment 8: *Are conclusions robust. We are not convinced that final conclusion is fully tested in a robust fashion. An important limitation is the disconnect between dissolved load changes and particulate concentrations at the riverine boundary condition. If it is implicitly assumed that PSP-Se does not*

change with load changes, that makes it almost inevitable that it is pragmatically impossible to reduce exposures below those seen in 1999. Ways to address that:

a. *Conceptual model with equations or terms listed.*

b. *Scenarios must manipulate PSP Se concentrations at the riverine boundary conditions. Capture high flow/low flow.*

c. *Test sensitivity to ocean end member; down to low value.*

d. *Important uncertainties. Good job of listing known/unknowns, but don't mention time. No data beyond 1999.*

e. *We hope that the the TMDL recommends research, monitoring and triennial review of important scientific uncertainties and what have we learned from science. Are knowledge gaps addressable with current technology.*

Tetra Tech Response: As noted above, numerous changes have been made to the report to address the effects of changing boundary conditions, to describe the scenarios in more details, and to describe the sources (e.g., Figures 4-31 – 4-33), and to describe the processes related to phytoplankton of dissolved species (e.g., Figure 4-8). Additional graphics and descriptions were added to enhance the conceptual model. For example, these additions have been made to this version of TM-6: representation of selenium exchanges between different compartments in each cell of the model (Figure 2-5), graphic depiction of the model cells and the representation of boundary conditions (Figure 2-9 and Box 3), and enhanced description of the concentration and flows used to compute loads (Figure 2-16).

Reviewer's Comment 9: *Green bar graph showing necessary reductions of particulate load shows huge reductions are required to meet targets. It is not transparent how this was done, even to we "experts". It must be explicitly and simply described because this is a major conclusion. In the meeting we heard that ug/g * gTSM = load. What happens if one a) starts with 1.5 ug/g at the riverine boundary, b) calibrate to the clam scenario wherein the data best fit (probably a lower IR) then c) reduced the concentration in river boundary condition in model by say half using the calibrated clam IR. Could you reach the target more feasibly? The most important conclusions are based upon this.*

Tetra Tech Response: This figure has been replaced with a more detailed description of the effects of changing boundary conditions and additional loading scenarios in Sections 4 and 5.

Reviewer's Comment 10: *It is also important to do the above seasonally. The conclusion about little responsiveness to loads must be done for low flows alone.*

Tetra Tech Response: In Section 5, the response of the system to changes in loading has been evaluated for seasonal variation and extremes in flow conditions.

Reviewer's Comment 11: *Choice of TTF-fish. Perhaps run with both 1.1 and 1.7 TTF for sturgeon in different scenarios.*

Tetra Tech Response: In Section 3.4, the model is run to compare predictions with data for white sturgeon muscle tissue, white sturgeon liver tissue, and scaup muscle tissue. There is variability in the model predictions based on variability in the clam concentrations. At this time, the simulations are performed with single

values of TTF (1.7 for white sturgeon muscle tissue and 1.8 for scaup tissue), although as the role of the modeling in the TMDL is finalized, additional runs could be performed with a range of TTFs.

Reviewer's Comment 12: *The choices of scenarios by the regulatory/stakeholder community will be critical in outcomes from the model and ultimately in conclusions about allocating sources of Se.*

Tetra Tech Response: The scenarios we have presented are illustrative, and intended to demonstrate model behavior. Specific loading scenarios can be run in a future phase.

Reviewer's Comment 13: *The model has helped us understand the data. Iteration should continue into the future.*

A5.3.4 Review of Technical Memorandum 6, John Oram, San Francisco Estuary Institute, Oakland, CA, April 3, 2009

Tetra Tech responses have been inserted following the reviewer's comments with this exact font and color.

Reviewer's General Comment: *Overall, the report is thorough, well-written, and interesting. The graphics are effective; they portray the information in a simple and clean manner. The authors are commended for drafting such a detailed report. Model development is well-documented and/or referenced. Enough information is given that the approach could be reproduced. Model testing was well-thought-out, executed, and documented. Results are effectively conveyed in writing and graphics. My specific critiques are as follows:*

Reviewer's Comment 1: *The document did not discuss the collective Delta sediment work of Lester McKee and Dave Schoellhamer (I believe it is McKee 2004). They have been observing sediment loads a Mallard Island for years. Their findings are relevant to how Delta sediment loads are handled in this model.*

Tetra Tech Response: The reviewer raised a good point. Particulate selenium loads from the Delta are important. We discussed the McKee et al. work in an earlier memo (TM2). However we agreed with the reviewer that the work is relevant here and should be discussed again in this document. In TM2, we used annual TSS loads from Delta estimated by McKee et al. (2006) and particulate selenium concentrations measured by Doblin et al. (2006) to estimate particulate selenium loads from Delta. The model used a function relating flow and TSS to estimated TSS concentrations and selenium concentrations on particulates to estimate particulate selenium loads. Our preliminary comparison of the data suggested loads estimated using the two methods agree relatively well. This is now shown in Section 2.10.

Reviewer's Comment 2: *Se in fish and diving ducks are the main drivers of the Se TMDL (correct?). Yet presentation of model results and model testing focused mostly on examination of physical parameters (e.g., Salinity, TSM, Se in water) and not on Se in fish and diving ducks. A stronger link between the physical parameters and Se in biota could be presented. It is difficult to judge if this model is appropriate without knowing how relevant certain findings are to the biota endpoints. For example, the model misses the ETM and Central Bay chl-a concentrations on relatively short time-scales. However, it is hard to say how important it is to get these features right without knowing how they effect biota*

concentrations. Bioaccumulation is not necessarily a fast process. If the shorter time-scale processes of the ETM don't affect biota Se concentrations greatly than missing the ETM is not that important. However, if the ETM is important to Se uptake by biota then the model needs to do better.

Tetra Tech Response: Selenium in fish and diving ducks were related to selenium concentrations in bivalves through several methods: linear regression relationships from Presser and Luoma (2006), a trophic transfer factor (TTF) and risk assessment approach.

We have now shown the model predicted selenium concentrations in sturgeon livers and surf scoter livers in Section 3.7. based on a more exhaustive analysis of the food web concentrations, it appears that the model does capture key features of the biological data, and that inadequacies in matching the peaks for TSM do not translate into systematic errors in tissue concentration predictions.

Reviewer's Comment 3: *Chl-a concentrations are predicted relatively well by the model. The biggest shortcomings are in Central Bay during late summer and early fall. There is speculation (by Cloern, Jassby, Oram, and others) that Central Bay phytoplankton blooms during this time of year could be driven by coastal upwelling outside the Golden Gate. Innoculation of Central Bay waters and/or transport of nutrient rich waters into Central Bay could play a large role in these blooms.*

My comment #2 applies here as well. It is hard to judge how important this is. I suspect it is important. We are talking about seasonal blooms that are relatively long-lasting. Certainly long enough for filter feeders to consume the phytoplankton and for zooplankton to graze.

Tetra Tech Response: The goal of the modeling is to represent the chlorophyll a concentrations with a small number of parameters, including growth and grazing rates which were driven by the same underlying forces for each year of the simulation. It is possible to adjust some of these parameters on a year-to-year basis, or to modify their spatial variation to more closely fit the data. This could help explain the selenium concentrations in biota, although there remains a data gap in that we do not have water column selenium data for all years of the simulation. Given the paucity of selenium data, our preference is to use a set calibration for this work, i.e., values are not adjusted locally to fit local peaks. This approach helps explain a considerable amount of the variability in the biological data over time (seasonally and inter-annually). Future work may consider some of these processes in more detail.

Reviewer's Comment 4: *Why was such a short time period used for model calibration (one year)? It is common to use roughly 60% of your observation data for model calibration and 40% for validation. It seems that model performance could be improved I the model were calibrated to a longer (and more diverse) calibration data set.*

Tetra Tech Response: The selenium speciation data are only available up until 1999. No speciation data exist after 1999. Speciation data for previous years 1997-1998 were used in model hindcast and represent different refinery load conditions.

Reviewer's Comment 5: *I have to say that the developers did a fine job of model testing. I am a big proponent of such tests, as they help build confidence in results. And in this case the testing results make intuitive sense, and thus build my*

confidence in the model. But, again, I am missing the link to fish and diving ducks. While the testing convinces me of the physics of the model and prioritizes data gaps for the physical model they do not tell me how important these data gaps are for biotic endpoints.

Tetra Tech Response: The model predicted selenium concentrations in livers of fish and diving ducks have now been added to the revised TM-6.

A5.4 ADDITIONAL COMMENTS RECEIVED FROM TRC AND RESPONSES PREPARED, JULY-AUGUST 2009

Additional comments on the Revised Draft TM6 document were received from three of the TRC members. Responses were prepared to these comments and together this information provided the basis for discussions at a teleconference meeting with the TRC, Tetra Tech and the Water Board (see Item 5 below).

A5.4.1 Comments on the June 19 2009 draft of Technical Memorandum 6, Nicholas Fisher, July 6, 2009

Tetra Tech responses are inserted in this color and font.

Reviewer's Comment 1: *I have read through the modifications of the document and think that most of the points I raised were adequately handled. The revised version which considers a range of selenite uptake rate values is an improvement. The conclusion that is drawn that remineralization rates need to increase in proportion (approx.) to increased uptake rates is interesting. It suggests future research that could be conducted to test this speculation, and that is one of the purposes of models (in my opinion). However, it is not clear to me that remineralization will result in release of selenite from cells. Since all the selenite that is taken up by cells is converted to organic selenides, the release of Se from cells will almost certainly be in the form of organic selenides, not selenite. The rate at which the released organic form gets converted to selenite is questionable, but data from the open ocean at least suggest that this rate may be very low. Looking at Cutter's data, in some open ocean waters the selenite levels can be far lower than the organic selenide levels. And speaking of remineralization, you note that "when riverine phytoplankton enters the bay, the selenium initially remains in the organic particulate compartment, and is mineralized over time." While this certainly strikes me as plausible (provided that the cells are not eaten first!), I am unaware of any published direct measurements that support this contention. Maybe I'm missing something?*

Tetra Tech Response: In the model formulation, the remineralization of particulate organic selenide results in releases of dissolved organic selenide, not selenite. The dissolved organic selenide is converted to selenite through an oxidation rate. The rate used in the model is set at a value of 0.004/day. Therefore, mineralization will result in organic selenide, which is slowly converted to selenite. This is now noted above Eq 23 on page 2-13.

The turnover of selenium by phytoplankton is considered to be quick (Fisher and Reinfelder, 1991). This quick turnover will allow intracellular and extracellular Se(II) pools to reach isotopic equilibrium (Baines et al. 2004). The release of organic selenide from the cells can be taken up again by phytoplankton. When riverine phytoplankton enter the bay, they may be grazed upon or go through processes that mineralize intracellular particulate organic selenide to dissolved organic selenide and uptake of dissolved organic selenide.

In one study (Vandermeulen and Foda, 1988), selenium release back into the medium by algae accounts for as much as 35% of the total selenium found in the external medium. After 10 days incubation, about 30.6% of labeled selenium was found in cells and 67.6% was found in cell-free filtrate for the Thalassionsira sp. For Cachonina sp., about 65.6% of labeled selenium was found in cells, while 27.5% was found in cell-free filtrates. In the cell free filtrates, 10.4% was found in live cell filtrates as selenite, while total amino acids, free amino acids and chloroform soluble forms account for 9.6%, 4.0% and 2.3% of the labeled selenium. Although the release of selenium metabolites from algae have not been measured in the field, it has been measured in the lab.

Reviewer's Comment 2: *Your point on the relative bioaccumulation of Se by different forms of algae is correct, but I fear slightly misleading. While the general*

order you note ("golden brown algae > dinoflagellates > diatoms > green algae") may be right, it is also worth noting that the data suggest that there can be big differences within groups–notably for diatoms, witness Skeletonema costatum vs. Thalassiosira pseudonana). Furthermore, data in Baines & Fisher (2001) suggest that the green algae are able to regulate their Se levels better than the other forms–not only are bioconcentration factors lower for these cells, but the absolute Se levels per cell appear to remain more constant over a 30-fold exposure range (0.15 nM vs. 4.5 nM selenite) (see their Fig. 3).

Tetra Tech Response: The general order is to provide only a rough grouping. We revised the text (p2-14) that different species of diatom can vary significantly, and that the grouping is an approximate guide.

We tested the influence of phytoplankton species on predicted particulate organic selenide concentrations and influence is large (section 4). When the dominant phytoplankton species is golden brown, predicted particulate selenium concentrations are closer to observed values.

Reviewer's Comment 3: *Partially for this reason, I still think that the determinations of particulate organic selenide would be very telling in terms of assessing the bioavailable Se potential for the bivalves. As interesting as it is to follow the bioconcentration of Se by different forms of phytoplankton (and near and dear to my heart), the ultimate story must be related to the total particulate organic selenide levels, provided that it is in particles that the bivalves normally can ingest (roughly 2-100 µm), depending on the animal. In other words, knowing the organic selenide levels in large seston "pieces" that are mm in scale would probably not be very useful.*

Tetra Tech Response: The temporal and spatial composition of phytoplankton species is not easy to model. Although we can make model runs representing a variety of species, any assumptions about the presence of specific phytoplankton species at any given time and place will be always problematic. If we make some assumptions of the dominant phytoplankton species with respect to time and space, we can do a simulation based on that assumption. Given the complexity in phytoplankton species with respect to time and space, it is difficult to make general assumptions with regard to the phytoplankton species. In long-term data collected in the bay, it has been noted that during wet and normal years, diatoms, greens, blue greens and chrysophytes dominate, while during dry and critically dry years, cryptophytes (golden brown), green flagellates and miscellaneous flagellates dominate (Lehman 1996). Therefore we can test a simplified scenario which assumes golden brown algae dominate during dry years, and green algae dominate during wet years. We can discuss this with the TRC, or include this in the proposed TM-7 which will contain additional model runs.

The point about the size classification of particulate selenium is valuable from the monitoring standpoint and is discussed in Section 6.7 on page 6-4 and 6-5 (Data needs).

Reviewer's Comment 4: *I have a question about the data presented in Table 2-1 and suggest a few modest changes to that table. It remains somewhat unclear to me why Reidel et al. (1996) measurements are used, since their experiments relied on wholly unrealistic Se concentrations (10 µg/l). The information shown in the 4th row, (uptake of dissolved selenite by phytoplankton), the top row within the box (for Riedel et al and Baines et al) gives uptake rates not adjusted for ambient*

Se concentrations. The bottom row within the same box shows the data normalized to ambient Se levels–however, this was not clear and I struggled for a while to understand how these data were produced from the original papers. Now, I understand them, but the document may benefit for further clarity on how these numbers were generated–perhaps a footnote to the table? Perhaps more importantly, the data for Baines et al. (2004) present data for microbial (mostly bacteria we believe) and phytoplankton uptake data (respectively, 0.2 - 1 µm and > 1 µm fractions). The data shown in TM6 only show the results from one of the two sample sites ("Channel" site) but fail to show the data from the other site ("Chlorophyll maximum"). There is not basis for excluding one of the sites, and I suggest that the table be revised to include them both. Keeping with the format as it stands now, the minimum uptake rate should be 0.15 [NOT 0.33 pmol Se/µg chl/hr]–that is, if both sites are included. However, I think it also valid to only include the phytoplankton data for this table (note that the descriptor in column 3 is "Uptake of dissolved selenite by phytoplankton." If only the phytoplankton (> 1 um fraction) are used, then the values range from 0.07 - 0.21 pmol Se/µg chl/hr. My calculations show that this translates to a rate constant of 225.8 - 777.8 l/g chl/hr, taking into consideration the ambient selenite concentration in each location and time (Table 1 of Baines et al., plus the added 0.03 nM of radioactive selenite).

Tetra Tech Response: We revised the table on page 2-10 to include data from both sampling sites.

The reviewer makes a good point that rates from Baines et al. when normalized to ambient selenium concentrations (which are more realistic to San Francisco Bay conditions) can be quite large (225.8 – 777.8 l/g chla/hr). We tested the model with varying selenium uptake and mineralization rates to illustrate the effects of using a different uptake rates on particulate selenium simulation (shown in Section 4.3). The test results suggested that when selenium uptake rates were increased to this rate, mineralization rates needed to be raised by approximately the same factor, in order to produce a reasonable selenium concentration on particulates. Thus, when uptake rates are high, the transformation of POrgSe back to selenate is not fast enough to predict a realistic selenate concentration in the bay. Reported mineralization rates for particulate organic Se (as you noted in comments above) are low at least in open ocean. Although the ambient concentrations used in Riedel et al. experiment are unrealistically high and for freshwater phytoplankton, they seem to produce reasonable selenium concentrations on particulates without using high mineralization rates. The values thus used were based in part on the literature and in part on the calibration.

With respect to values cited from Baines et al. (2004), we included the value for the channel site at first simply because the site has a phytoplankton level closer to the conditions in the bay (2 µg/L) rather than 12-30 µg/L observed in the other study site ("chlorophyll maximum"). The rates measured when normalized to chlorophyll a concentrations however are similar between the two sites. When estimating the uptake rates, we include both phytoplankton uptake and bacteria uptake for the reason that some bacteria uptake may also exist in the Bay and could contribute to high particulate selenium concentrations. However, since we are comparing only phytoplankton uptake rates here, we could make the changes to include phytoplankton uptake only. Section 4.3 has been updated to reflect this discussion.

A5.4.2 Comments on the June 2009 draft of Technical Memorandum 6 by Regina Linville, August 12, 2009

Tetra Tech responses are inserted in this color and font.

Tetra Tech Response: We thank the reviewer for her thorough assessment of our report and associated comments. A principal concern raised in this review is related to the relative magnitude of particulate selenium that is present as permanently suspended particles (abbreviated as PSP and generated primarily in the riverine sources) versus that present in living phytoplankton. PSP is comprised of inorganic and organic components including planktonic detritus. It is the reviewer's point that much of the particulate organic selenium in the bay is associated with phytoplankton, and that, at the very least, we are overestimating the contribution of organic selenium in PSP in the model development. Our primary response, explained in more detail below, is that the relative magnitude of the phytoplankton selenium and PSP-selenium is based on the best data we have, and is significantly constrained by the calibration of the model, where concentrations for multiple selenium species, both dissolved and particulate, were matched to observations in the bay.

Reviewer's Comment 1: Particulate organic selenium in permanently suspended particles. *Particulate organic selenium (Se) in permanently suspended particles (PSP) appears to be overestimated in this model. In conceptual models of the bay, particulate organic Se is mainly considered to be associated with living phytoplankton. In TM6, particulate organic Se enters NSFB from the rivers as both PSP and phytoplankton. Based on discussions with the authors, particulate organic Se associated with PSP is assumed to be Se in detritus. In a separate model calculation, riverine particulate organic Se associated with phytoplankton is estimated based on chlorophyll-a (Chl-a), carbon to Chl-a ratio and Se to carbon ratio.*

Tetra Tech Response: We do not think that particulate organic Se is mainly associated with living phytoplankton. The reviewer didn't provide a reference for the statement "In conceptual models of the bay, particulate organic Se is mainly considered to be associated with living phytoplankton," which would be helpful to our work.

Note that lab tests with bivalves and different forms of particulate selenium have shown assimilation from living and non-living sources (Table 2-4 in TM-6 report and references cited therein).

As measured by Doblin et al. (2006), chlorophyll a (representing living phytoplankton) is at approximately the same concentration of phaeophytin indicating the presence of relatively high level of detritus. Total particulate organic carbon measured in the estuary is only accounted for by 20-30% of carbon associated with living phytoplankton. Therefore in the model, we assumed particulate organic Se to be associated with both living phytoplankton and detritus. And a large portion of the living phytoplankton and detritus in the Bay enters from the Delta.

Particulate organic Se in PSP (defined as permanently suspended particles) was derived as the difference between total particulate organic Se and particulate organic Se associated with phytoplankton. Therefore it is unlikely to be overestimated unless phytoplankton associated particulate organic Se is underestimated.

Reviewer's Comment 2: *The example in Table 1 of these comments (see Appendix 6) shows that PSP-associated particulate organic Se (detritus) has a very large impact on overall particulate organic Se concentrations in the model. Using the average flow of November 1999, an estimated PSP concentration of 0.010 g/l and the model parameters for Se associated with PSP (Table 3-3 of TM6), the amount of particulate organic Se contributed by riverine PSP is 56 g/day. Using the same flow rate, a Chl-a concentration of 1.2 µg/L (approximate mid-point of Nov 1999 Delta samples in Doblin et al., 2006) and the Baines et al., 2004 conversion of 15.9 ug Se/g C – the particulate organic Se load from Sacramento River phytoplankton is 33 g/d. In this example, the particulate organic Se contributed by riverine PSP (56 g/d) is greater than that of riverine phytoplankton (33 g/d). [Note, I used an approximate median value for low-flow Chl-a from Doblin. Using the complete range of low-flow Chl-a observed by Doblin, the phytoplankton Se contribution varies from much lower than to greater than that of PSP particulate organic Se].* ***And most importantly, the particulate organic Se associated with PSP is defined by the riverine concentration throughout the entire estuary (eq. 23).*** *The concentration of particulate organic Se associated with PSP is mainly impacted by the rate of mineralization to dissolved organic Se (k1), which is relatively small (0.0066/day).*

Tetra Tech Response: The reviewer used single day values to illustrate that PSP-associated particulate organic Se (detritus) is higher than the phytoplankton associated Se. This is not how the two sources are accounted for in the model. Both PSP and phytoplankton concentrations from riverine sources can vary through time. The date selected by the reviewer reflects a relatively low Chl a concentration of 1.2 ug/L. As shown in Figure 3-8 of TM-6, observed Chl a concentration by Doblin et al. at the head of estuary were at higher concentrations of 4 ug/L for many of the months. As a result, the estimated particulate organic Se associated with phytoplankton could be much higher than 33 g/d for other dates. Tables 1-5 from the reviewer were included in the Appendix (see page 26 in this document).

The reviewer is concerned about the fraction of selenium associated with organic forms. Living phytoplankton carbon accounts for only 20-30% of particulate organic carbon (POC) measured at Rio Vista by Doblin et al. (2006). Therefore, other sources of POC (e.g. detritus of plant material, microbes) make a significant contribution to the fraction of Se associated with organic forms (POrgSe).

Eq. 23 computes a mass loading of particulate organic Se from the river that is added to the Se pool in the estuary (on daily basis), once in the estuary, it is subject to transformations such as mineralization and uptake (in addition to transport advection and dispersion). We labeled the terms in Eq.23 that are associated with riverine inputs. Eq. 23 represents inputs from rivers and in-situ transformations.

We revised section 2.5 (p 2-11) to clarify these points.

Reviewer's Comment 3: *Figures 4-20 and 4-21 of TM6 help to clarify my concern here. These figures show the simulated particulate Se in the estuary due to PSP, suspended bed sediments (BEPS) and phytoplankton in both ug/L and ug/g. Tables 2 and 3 of these comments show my estimations of the relative sources of particulate Se* ***assimilated into clams*** *based on the simulations shown in Figures 4-20 and 4-21. My method for estimating these values is explained in the*

footnote.1 In Figure 4-20, the spatial distribution of particulate Se is simulated using November 1999 estuary conditions (low flow). It appears that particulate organic Se from PSP accounts for roughly 22 – 31% of the total Se assimilated by clams and 37 – 46% of the organic Se assimilated (see Table 2 here). Figure 4-21 provides simulated particulate Se concentrations at Carquinez Strait during high and low flow (see Table 3 here). High flow (June 1998 & March 1999) particulate organic Se from PSP accounts for roughly 39 & 45% of the total Se assimilated by calms and 61 & 82% of the organic Se assimilated. Particulate organic Se in PSP does not change very much in the modeled estuary so the large contribution of particulate organic Se from PSP will minimize the impact of decreased Se concentrations in phytoplankton. By freezing a large proportion of organic Se, I think the model loses the ability to detect small but relevant changes in particulate Se. (Note: the estimates of particulate organic Se associated with PSP at greater salinities will likely be artificially high because selenite is absorbed onto PSP as it passes through the estuary. The main point here is that the organic Se associated with PSP does not ***decrease*** *very much after it enters the estuary.)*

Tetra Tech Response: Sediment contribution of selenium originates from two sources: sediments entering the estuary from the rivers and sediments generated from bed exchange processes in the estuary. The riverine inputs of suspended sediments and sediment contribution from bed exchange are treated separately in the model. Also, composition of selenium in these two sources of sediments is likely to be different. Figures 4-20 and 4-21 show the concentrations of total particulate selenium from river PSP, bed exchange sediments and phytoplankton.

Riverine suspended sediments contain particulate organic selenide, adsorbed selenite + selenate, and elemental selenium. Sediments from the bed are dominated by elemental selenium; however they also contain a fraction of particulate organic selenide and adsorbed selenite + selenate. The sediment contribution often referred to in other references is the sediment contribution from bed exchange only.

The load inputs of sediments from the Delta to the Bay have been estimated by other investigators to be large sources, ranging from 0.26 to 2.6 Mt/yr (McKee et al. 2006). USGS water data reports provide estimates of the annual suspended sediment load measured at Freeport. For water year 07-08 the sediment load was ~0.3 Mt/yr while for 05-06 water year it was ~2.9 Mt/yr. These studies suggest that the amount of selenium associated with suspended sediment from the Sacramento River can be large and highly variable. Selenium associated with this large sediment source can be overlooked. We don't think the particulate selenium associated with detritus is out of place. Detritus concentrations measured by Doblin et al. (2006) as shown in Figure 4-41 of TM-6 first decrease but then increase toward the seaward boundary.

Additional clarifications are identified below:

1. The contribution of selenium from bed sediments through bed exchange (erosion) is an independent process from riverine inputs of suspended sediments. When estimating roles of sediments to particulate selenium, these two processes should be separated, as in Doblin et al. (2006).
2. The increase of particulate organic Se through the estuary (or limited decrease) is supported by the observed data (Figure 3-26 of TM-6). Particulate organic selenium measured by Doblin et al. (2006) showed an increasing trend through

the estuary. Whether this increase is due to fast mineralization of particulate organic selenium to dissolved organic selenium and rapid uptake by phytoplankton to form living particulate organic selenium or slow mineralization, the observed particulate organic selenium concentrations (in µg/g) increase through the estuary. Moreover, the uptake of selenite and organic selenide is higher than other species of selenium. A fast turnover of particulate organic selenium needs to be balanced by relatively fast selenium uptake rates to maintain the particulate organic selenium concentration. When uptake rates of selenite exceed 10x the rates used in the model, the transformation of selenite is limited by the oxidation of organic selenide to selenite. This, in turn, will result in predicting lower selenite concentrations than observed in the Bay (Figure 4-10 of TM-6).

3. The PSP associated particulate organic selenium is not fixed by the riverine particulate organic selenium concentrations. The relatively slow mineralization rate was derived through balanced calibration and is within the literature range (k1, Table 3-3 in TM-6).

Reviewer's Comment 4: Simulated Selenium in Phytoplankton. *In the model, riverine (freshwater) phytoplankton continues to grow and uptake Se throughout NSFB. The likelihood of this actually happening is highly dependent on flow, since most freshwater phytoplankton species have limited salinity tolerances. During lower flows, many riverine phytoplankton species will be affected by increased salinity in NSFB and will not continue to function (i.e., take up Se). Treating riverine phytoplankton as estuarine phytoplankton is likely to overestimate the influence of the Sacramento Rv. during lower flows.*

Tetra Tech Response: The model simulates overall phytoplankton concentrations, as represented by chlorophyll a in the estuary by season relatively well. As discussed in the model evaluation section, variations in phytoplankton concentrations by season show good agreement with the measured data (Figure 3-23 of TM-6). Therefore the overall phytoplankton concentrations during low flow are not over-predicted.

The reviewer suggests that during low flow conditions (higher salinities) freshwater phytoplankton may not be able to function. This is true. Indeed, across any spatial and temporal gradient in the estuary changes in the species of phytoplankton occur and a shift from freshwater to marine species is common. More subtle shifts in response to water chemistry and temperature are also taking place. The model does not represent the inter-species dynamics of algae in the Delta and bay. Both freshwater and marine phytoplankton is represented in the model as "one compartment" and these are tracked through the chlorophyll a levels.

The observed phytoplankton concentrations may be lower during low flow and these concentrations are reproduced well by the model. The selenium associated with riverine phytoplankton inputs is still accountable as riverine contribution, regardless whether it remains as living phytoplankton or detritus after it enters the estuary. The contribution of riverine phytoplankton selenium is estimated as loads of selenium associated with phytoplankton entering from the rivers. The model formulation section related to this topic (Section 2.6) has been edited to reflect this discussion.

Reviewer's Comment 5: *Potential load reductions scenarios will not impact Se loading from Sacramento Rv. phytoplankton. Is there a way to limit the active uptake of Se by riverine phytoplankton to freshwater areas in the model (i.e., link it with flow)?*

Tetra Tech Response: It is possible to limit riverine phytoplankton uptake of selenium to the freshwater area (e.g. at salinity < 1.0) by changing the uptake rates. However we still need to simulate uptake of selenium by marine phytoplankton, as long as there is phytoplankton in the estuary. Passive uptake of selenium by phytoplankton is also possible (Riedel et al. 1996). In the model, phytoplankton are treated as a single component and not treated as two groups of species (marine and freshwater). The reasons behind this simplification are explained in Section 2.6.

Reviewer's Comment 6: *Additionally, the explanation of uptake rates of dissolved Se by phytoplankton (k4 – k6) is unclear. Uptake rates from Riedel et al. (1996) and Baines et al. (2004) are shown in Table 2-1 using different units. The significance of the different units and justification of the choice of rates needs clarification.*

Tetra Tech Response: The uptake rates are shown in both the units reported in the original papers and using a uniform unit (shown in parenthesis; l/g chl a/hr). We chose to show the rates in original units for easy comparison to the original references and also showed the two rates in common units for comparing rates from these two sources.

We revised the text to reflect this point (p 2-9).

Reviewer's Comment 7: *Considering that the measured uptake of Se in different phytoplankton species varies by an order of 10^5, and the model is not able to capture changes in phytoplankton composition, is this approach truly an improvement over the simplified approach developed by Presser and Luoma (2006)? I think this is a very important question to consider.*

Tetra Tech Response: The model provides a framework for testing the influence of changing phytoplankton composition, even though the current parameterization is limited by knowledge of phytoplankton species composition and selenium concentration in species in NSFB.

The model also provides mechanisms to simulate spatial and temporal variations in phytoplankton concentrations through the bay, which is not easily achieved by the simple model. In addition, selenium dynamics are not determined by phytoplankton alone. The model provides mechanisms to simulate constituents such as salinity and TSM, and loads and different species of selenium (particulate organic, particulate elemental, particulate adsorbed selenite + selenate, dissolved organic selenide, selenite and selenate).

The model is compared to the Presser and Luoma results (Section 5.3). The discussion in Section 5.3 and in the new Section 6.7 is updated to reflect the pros and cons of using a more complex model.

Reviewer's Comment 8: Boundary Conditions *- Riverine Boundary. I am still unclear regarding the authors choice of the Se to carbon ratio (Se:C) used to simulate organic Se concentrations in riverine phytoplankton. The selected Se:C of 15.9 µg Se/g C from Baines et al. (2004) is much higher than the range of < 1 to 4.4*

µg Se/g C from cultured phytoplankton in Doblin et al. (2006). Doblin exposed the phytoplankton to 90nM Se or ~7µg Se/L, which is higher than concentrations found in NSFB. However, it appears that the uptake rate of selenite into phytoplankton (k4) was based on a study using 10 µg Se/L. Is there an additional reason for omitting the Doblin data (or using a combination of the Baines and Doblin data)?

Tetra Tech Response: Se:C ratios, as suggested by previous studies, vary greatly by species (Baines and Fisher, 2001; Doblin et al. 2006). Therefore a Se:C ratio measured in the Delta was considered as the best data available to determine the amount of Se associated with phytoplankton entering the estuary through the Delta. The value of 15.9 (measured by Baines et al. 2004) is well within the range reported by Baines and Fisher (2001) of 0.22 to 30.4 µg/g under the 0.15nM experiment and 0.05 to 217 µg/g under the 0.45 nM experiment. The ratio reported in Doblin et al. (2006) is the atomic ratio (not mass ratio) and a unit conversion from atomic ratio to mass ratio is needed. Based on the molar weight of Se and C, a conversion factor of 78.9/12 was used to convert these atomic ratios. The results for Se:C in µg/g are shown in Table 2-2 of TM-6. These suggest that measured Se:C ratio by Doblin et al. (2006) of 3 to 13.49 (dinoflagellates) µg/g, instead of <1 to 4.4. We added this note in the text (p 2-14).

Reviewer's Comment 9: *In TM6, the authors note that "Model-predicted selenium concentrations in phytoplankton (in terms of Se:C ratio) were compared to observed values in the seston of the Delta (Baines et al., 2004). The Se:C ratio in phytoplankton is calculated as selenium concentrations associated with phytoplankton (µg/L) divided by phytoplankton biomass (in units of carbon, g C/L)." Baines et al. used a C:Chl-a of 28 to estimate a Se:C of 12.05 x 10^{-6} in the Delta. This was compared to a Se:C of 15.9 x 10^{-6} in uptake experiments using delta samples. The model reviewed here uses a C:Chl-a of 51 to estimate Se:C in phytoplankton, which would have resulted in a much higher Se:C in the Delta and a less favorable comparison to the experimental Se:C in Baines et al.*

It is not clear to me why the carbon to Chl-a ratio was set as 51 mg C to 1 mg Chl-a following Cole and Alpine (1991) instead of 28 mg C to 1 mg Chl-a following Cloern et al 1995 (as was used by Baines et al, 2004). Also Cole and Alpine (1991) is not included in the references and I have not seen that paper. The C:Chl-a ratio has a significant impact on simulated riverine phytoplankton Se since each gram of carbon represents 15.9 µg organic Se.

Tetra Tech Response: The reference should be Alpine and Cloern (1991) and has been corrected in the table. The ratio of 51 is for freshwater phytoplankton and is based on an average of the measured carbon uptake rate. We recognize that this ratio varies in time and space and a wide range is possible. The value of 28 in Cloern et al. (1995) is a modeled value for a single day in June 1993. Ideally, a model of phytoplankton could include the growth-rate impact on the C:Chl a ratio, but this was beyond the scope of the selenium modeling. The text has been modified accordingly (p 2-45).

Reviewer's Comment 10: Boundary Conditions *- Seaward Boundary. The seaward boundary for particulate Se is much higher than all other observed data. Other TRC members have voiced concern regarding the use of this boundary condition. This parameter has a large impact on the model outcome and should be reconsidered.*

Tetra Tech Response: As a result of discussion at the TRC meeting in April we tested different seaward bound particulate Se concentrations and revised the model seaward boundary concentrations to fit the observed data (~0.8 – 1.0 µg/g) at Golden Gate by Doblin et al. (2006). Figure 3-26 and Figure 3-42 show the comparison with the observed data.

Reviewer's Comment 11: Bioaccumulation in Bivalves: *As described above, my estimation of the relative sources of modeled assimilated Se in clams is shown in Tables 2 and 3. These estimates are based on model simulations shown in Figures 4-20 and 4-21 in TM6 and are described in the footnote of these comments. In the model, approximately half of the Se assimilated by bivalves originates in PSP during low flow, while 71 – 82% originates in PSP in high-flow simulations. In a low-flow simulation, the relative sources of assimilated Se in bivalves are estimated as: sediment 23 – 46%, detritus (organic fraction of PSP) 22 – 31% and phytoplankton 29 – 48% (Table 2). In the high flow simulation, the relative sources are estimated as: sediment 36 – 45%, detritus 39 – 45% and phytoplankton 10 – 25% (Table 3: June '98 & March '99). This does not agree with my understanding of Se dynamics in NSFB. In most conceptual models, the bioaccumulation of Se in NFSB is driven by phytoplankton. In this model, bioaccumulation is mainly driven by nonliving material entering from the Sacramento Rv. The high level of particulate Se modeled for detritus is particularly out of place. Detritus generally decreases from the confluence of the rivers to San Pablo Bay, but most of the Se in detritus is maintained throughout the estuary in this model. I think there is evidence that detritus is not present at consistently high levels throughout the estuary. Additionally, the assimilation efficiency of 0.8 for particulate organic Se was determined using living phytoplankton -- the assimilation of Se in detritus could be significantly different. Most importantly, as mentioned above, load reduction scenarios do not impact the organic Se fraction of PSP – essentially locking in a highly bioavailable, and flow dependent, parameter in the model.*

Tetra Tech Response: Please see response to Comment 3 where this issue is addressed in more detail.

Besides the prior comments, another conceptual model of the bay (Abu Saba and Ogle, 2005) also noted the importance of upstream riverine and Delta sediment inputs: "upstream riverine and Delta sediments and Delta primary productivity are major sources of the suspended particulate selenium".

The assimilation efficiency of particulate organic selenium has not been determined for nonliving particulate organic selenium; however this form of particulate organic selenium exists in the estuary.

We added these discussions to p2-11, p4-38, and p2-18.

Reviewer's Comment 12: *Similarly, the role of sediments in bioaccumulation appears too large in this model. The assimilation efficiencies of sediments are 0.45 and 0.2 for the selenite/selenate and elemental Se fractions. In this model, sediment is a large source of assimilated Se in clams (up to 46 percent of total assimilated). Considering the relatively low assimilation efficiencies of sediment, the clams are assumed to ingest huge amounts of sediment particles. Clams are herbivores and need to consume enough plant material to survive. Many species*

of clams have efficient mechanisms to avoid ingesting large volumes of sediment (e.g., pseudofeces or retracting siphon).

Tetra Tech Response: The assimilation efficiencies are based on particulate Se species, regardless of their sources. The reviewer suggests that sediment contribution is too large and that the PSP contribution is also too large. If both are true, this would only suggest that the contribution from phytoplankton is underestimated, based on total observed particulate selenium. However, the phytoplankton concentrations were simulated well by the model. The Se:C ratio used in Delta phytoplankton of 15.9 µg/g and Se:C ratio of 51 were both considered as too high by the reviewer. This would also suggest that the phytoplankton Se is overestimated and not underestimated.

Again we think the role of sediment contribution may be overestimated in the calculations from the reviewer. The bed sediment also contains some organic selenium (Table 2-11 of TM-6) which was taken to be all inorganic by the reviewer. Thus, by adding Se from riverine suspended material and bed sediment, the estimated contribution is actually for inorganic particulate selenium.

The assimilation efficiency has been found to be relatively high for bacteria plankton (possibly present in PSP) (Werner and Hollibaugh, 1993).

If there is quantitative data that clams feed exclusively on living phytoplankton and avoid mineral sediments, we could revise the uptake rates for different sources of particulate selenium.

Reviewer's Comment 13: *The above issues are very important in relation to the simulated swamping effect of the Sacramento River. PSP from this river appears to control the model, yet this parameter is built on a fairly crude estimate of suspended material in NSFB. PSP is a function of a limited number of measurements of total suspended material (a measurement with high temporal variability) and flow rates. The Se contained in PSP is a function of calibration coefficients that fall within a very large range of observed data. The calibration is based on one year of data with limited observations. There is huge room for error in the simulation of PSP yet, because of the complexity and specificity of this model, an air of precision is associated with model predictions. In TM6, this is supported by testing the model using the limited data that falls outside of the calibration data set. The results are promising for a complex model, but level of uncertainty and variation in the model does not support the level of precision conveyed in the conclusions of TM6.*

Tetra Tech Response: We agree that PSP is an important parameter in determining selenium inputs to the bay. However, this is not the only parameter that controls the model output.

PSP as a function of flow is able to capture the range of variation observed in TSM. Observed PSP concentrations at the Rio Vista do not seem very sparse (as shown in Figure 2-12 of TM-6). Alternatively observed PSP concentrations can be used in model inputs, however, this will likely limit the use of the model for future projections with flow changes because PSP is likely to vary with flow.

The model calibration was done using the available data. If more data become available in the future, it will surely help reduce the uncertainties and improve the model simulations. The calibrated values fall within the range of the observed data; the calibrated parameters are the best fit value that can be used to estimate

particulate selenium for future conditions. Although the precision is limited by the large variation in observed data, the standard deviation of the estimated parameters can be used to derive confidence intervals of the model predictions.

We agree there is variation in particulate selenium in riverine inputs, and the variation is likely to be associated with flow and the relative contribution from the two rivers. Therefore different boundary conditions may be used for different flow conditions. For a particular day, the variation seen in particulate selenium in the estuary is not likely due to variation from riverine inputs but rather in-estuary processes given the residence time and this in-estuary process can not be easily captured by a 1-D model. We added some of these discussions to the report (p3-46).

Overall, a model such as this offers a representation of the processes that are understood to be important. It is a tool for analyzing the behavior of selenium in NSFB, and creates a framework for additional data collection. That some features of the data are not fully captured is important to point out, but the solution is to try to improve the existing model and/or calibration. Replacing the model with a simple linear partitioning coefficient does not enhance understanding or serve to guide future monitoring. There is new discussion of this issue under the "Discussions" section (6.7).

Reviewer's Comment 14: Bioaccumulation in Predators - *Figure 3-36 is unclear to me. When discussing the hazard quotient (HQ) of Se exposure to predators, I'm still unclear on your statement that "a large number of conservative assumptions that are incorporated in the estimated HQs and a value slightly greater than 1 does not indicate significant risk." What are the conservative assumptions applied in the estimation of HQ? If the assumption that sturgeon and diving ducks feed exclusively on Corbula is considered conservative, what other NSFB species do you consider as significant food sources for these predators?*

Tetra Tech Response: We consider the assumptions used as conservative because:

1. The diet is assumed to comprise only Corbula amurensis, which bioaccumulates selenium most efficiently.
2. The predators were assumed to be present in SF Bay 100% of the time, which may not be true due to migration.
3. The HQs computed were not seasonal or annual averages, but estimated using daily estimates of clam concentrations, which showed clear peaks. Annual average HQs would be lower than the peak HQs that are shown.

The text of this section has been modified to explain what we mean by "conservative assumptions." (p2-23)

Reviewer's Comment 15: Summary and Conclusions: *In summary, I am concerned over the limited review of specific functions in this model. The TRC review process has been lengthy, but has focused on general concepts leading up to the actual (empirical) model. In April 2009, the TRC members did not understand how the model was functioning. The revisions to TM6 did not address several of the specific concern raised at the April meeting.*

Tetra Tech Response: We respectfully disagree with the reviewer's view of the TRC's level of understanding of the model and the extent to which concerns raised by the TRC were addressed in the revised TM-6. The comments received on the revised TM-6 from other TRC members do not concur with the reviewer's opinion.

Reviewer's Comment 16: Summary and Conclusions*: My specific concerns focus on the treatment of particulate Se and the impact of that treatment on bioaccumulation. The model concludes that load reductions would not decrease particulate Se concentrations due to the overwhelming input of the Sacramento River. This concerns me because it is different from our current understanding of Se dynamics in NSFB. When the influx of the Sacramento Rv. is lowest (lowest flow period during low flow year), the Se concentrations in bivalves are the highest. When the influx from the rivers is highest, the bivalves contain significantly lower Se concentrations. In the scientific literature, this is generally related to longer residences times during low-flow and thus greater uptake of Se in phytoplankton. In the model, increased bivalve concentrations during low flow are driven by PSP from Sacramento Rv., while decreased bivalve concentrations during high flow result from higher volumes of sediment diluting the food source of the clams. At least, this was my understanding from talking with the authors.*

In conclusion, I suggest caution in the continued use of this model. The model was highly calibrated to fit a limited set of data. When compared to other limited data sets, the variation and uncertainty is too high to support the level of precision presented in the conclusions of TM6. The drawback of using complex models that are based on very limited data is the potential for overestimating the ability to predict events in the modeled system. On the other hand, the benefit of using simplified models to describe limited data is that the uncertainty of the predictions remains clear. I suggest that you reconsider using the simplified modeling approach presented by Presser and Luoma (2006) to set initial load reduction targets and improve the model described in TM6 with additional data over time.

Tetra Tech Response: We think the contribution of particulates selenium from riverine sources cannot be overlooked, given the large amount of sediment inputs estimated from the Delta by other independent studies. We added this discussion to the text (p 2-11).

Riverine inputs, as estimated, were only a fraction of the total particulate selenium. When riverine inputs are low, the control of dissolved selenium in the estuary can result in changes in particulate selenium concentrations (Figure 5-4 of updated TM-6). Given the right combination of conditions (low flow-> low riverine input and high Chl a concentration) the changes in dissolved selenium will result in uptake into particulate selenium and these transformations can be significant.

We are a little unclear about the comment that the current understanding of selenium dynamics in NSFB is different from the results.

The model provides temporal and spatial variation of simulated selenium in particulates and bivalves that has not been achieved by a simple partitioning model. It also provides spatial and temporal variation of loads going into the estuary. Moreover, it gives consideration of speciation effects from different sources of selenium and the uptake of selenium by phytoplankton and bivalves depends on simulated selenium concentrations by species. Although limited by data in some areas, the model uses the best information available today and assembles the most current scientific understanding of selenium biogeochemistry

in this estuary. Ultimately it is up to the Water Board to decide what model to use. We think the model described in TM-6, with its assumptions clearly stated is sufficiently robust to be used as part of the decision-making process for the selenium TMDL.

A.5.4.3 Comments on the June 19 2009 draft of Technical Memorandum 6, Samuel N. Luoma, July 6, 2009

Tetra Tech responses are inserted in this color and font.

Reviewer's General Comment: *The changes in the report, overall, have really improved its transparency and understandability. The improved executive summary does an excellent job of explaining the calibration, evaluation and predictive modes in which the model is developed and employed. The addition of moderated language and detail about predictions, as well as the discussion of limitations and assumptions is an important improvement. Discussion of sensitivity to assumptions about the Sacto River, under current discharge conditions, and the call for more data in this regard is also quite valuable. In the report, the section on boundary conditions is another very important addition that adds greatly to the clarity of the document, as does Figure 2-16. As I will note below, I do not believe that the chosen boundary conditions represent the Bay's true boundary conditions, but because they are well explained they are acceptable as long as they are not mis-used (see below).*

The advanced simulations under different boundary conditions represent a great deal of work and are also quite valuable. It was important to show the degree to which dissolved and particulate Se are most sensitive to riverine input parameters and that particulate selenium concentrations are sensitive to selenium content on particulate material at the head of the estuary. The details of the simulations were insightful. The scenarios are also informative and more robust than in earlier reports.

I really only have one serious objection to the present document. It boils down to Scenario 10 and it is serious because it represents a long standing point of contention in the ongoing disputes about Se in the Bay. One of the bulleted conclusions seems to build from this and it has serious implications, if taken to an extreme, for the TMDL. If I understand the model correctly, Scenario 10 uses the particulate Se boundary conditions specified earlier in the report. These use particulate Se data from Doblin for the landward concentrations taken from stations that are, in fact, within the tidal influence of the Bay (i.e. Bay particulates, not river particulates during a time when the Bay was more contaminated than it is now). What I read scenario 10 to say is that if point source loads are removed and local tributary loads are removed and the SJR dissolved Se drops to 0.2 ug/L there will still be no change in Se concentrations in the bivalves? What is not stated, if I am correct about the boundary conditions, is that conclusion is valid only if particulate Se stays at 1999 levels. Doesn't this assume that the drop in dissolved Se that the model predicts under these circumstances,

will not be accompanied by a decrease in particulate Se. In fact, under these conditions shouldn't particulate Se at the riverine boundary be almost the particulate Se in the Sacramento River (for which we have no data, but it surely is among the lowest of the Doblin numbers, not the average – about 0.05 ug/g). It is a self-fulfilling prophesy that the bivalve Se will not go down as long as particulate

Se does not go down. With a Kd range of 10^3 to 10^4 in every instance where particulates and dissolved Se it seems logical to assume that a drop in dissolved Se will result in some effect on particulate Se in the long run. The way Scenario 10 is presented it allows the politically volatile and, in my view, illogical conclusion that Se inputs to the Bay make no difference to bivalves; in essence the implication is that the contamination of the Bay is the fault of C. amurensis, despite the fact that the contamination in predators preceded the invasion of this bivalve. In fact one of your conclusions still hints at this (see below). This of course could easily lead to the further conclusion that adding Se back to the Bay will have no effect on contamination of the food web. If that is the conclusion of the model, then I think it should be stated clearly so it can be debated. But that conclusion is purely a function of the boundary conditions of the model that I just stated, unless I completely misunderstand them, which I don't believe is true. This report is a vast improvement over earlier editions and is becoming quite an impressive document. But to finish with a conclusion that goes back to the same old arguments with the same old origins seems unconstructive.

Tetra Tech Response: Scenario 10 when looked at closely resulted in some changes in particulate selenium concentrations and Se concentrations in bivalves. When point source loads are removed and the SJR loads are reduced to 0.2 µg/L, the particulate selenium concentrations decreased by 0.05 µg/g and Se concentrations in bivalves decreased by 1.2 µg/g. Gridlines were added to Figure 5-4 and Figure 5-5 of TM6 to show the difference among the scenarios. It is possible to run a scenario with a much lower value of particulate Se as the boundary condition at the riverine end than observed in 1999. Indeed, scenarios with a wide range of boundary conditions were presented in Figure 4-16.

We can discuss with the TRC what this boundary condition could be and re-run the simulation. Note that there are no data that could be used to define this condition. The current values were used because the Doblin et al. analysis did not show values at Rio Vista dropping very low even when the salinity was low (suggestive of conditions with minimal bay influence).

Reviewer's Comment 1: Minor points and a couple points of interest: *There are many scenarios that could be run with the model. They do not have to be done now, but it would be interesting to include that in future needs. For example, what happens when change proportional contributions of two rivers to the Bay by greatly cutting Sacto inputs and using values from Vernalis as if no diversions? Halve Sacto and triple SJR simultaneously = worst case but maybe a Peripheral Canal case.*

Tetra Tech Response: We ran a scenario with increased flow to Vernalis flow without cutting Sacramento River flow and it appears to result in changes in particulate selenium (as in TM6). We tested a scenario of half Sacramento and triple SJR (see Figure 1 below). Additional scenarios are planned to be run in a separate TM (TM-7), once there is agreement on the approach used in TM-6.

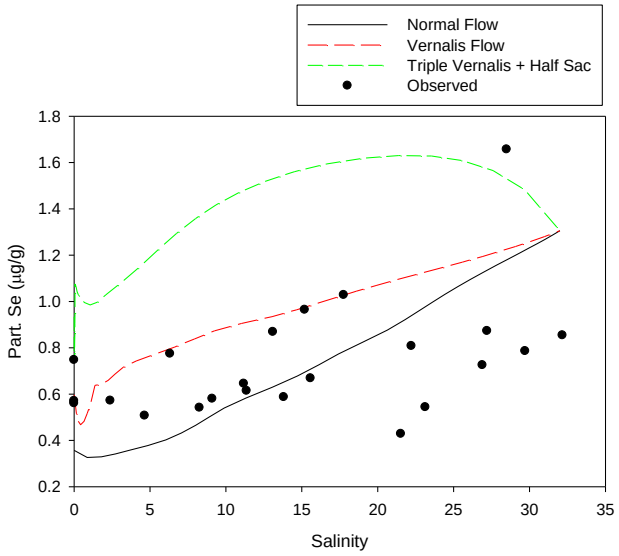

Figure A.5-1 Simulated particulate selenium under the scenarios of increasing SJR flow input to Vernalis River flow and increasing SJR flow to triple Vernalis flow and half Sacramento River.

Reviewer's Comment 2: *Page xviii, end of paragraph 1 seems an important sentence but it is confusing. Paragraph 2 is very important to future water management strategies. Be sure these are clearly stated.*

Tetra Tech Response: The sentence at the end of paragraph 1 was not well-worded. Here is what we now say: "The finding that particulate concentrations are relatively insensitive to decreases in dissolved selenium loads particularly during the high flow season, is significant from the standpoint of the TMDL process."

Reviewer's Comment 3: *As discussed above, the bulleted statement: "The current assessment of risk to predator species in the bay from selenium uptake is largely a result of the presence of Corbula amurensis, despite the two-decade long efforts to control non-point sources in the Central Valley and point sources in the bay." What does this mean? Surely you are not implying that there is no effect from source inputs to the Bay…that what we have always seen is background concentrations in C. amurensis? How does this square with declining concentrations over recent years? With the fact that predators were contaminated to a similar degree pre-invasion of C. amurensis. How about: "The risks to predator species in the bay from selenium uptake are very sensitive to changes in particulate concentrations because of the presence of C. amurensis, an organism that bioaccumulates Se strongly when small changes in particulate concentrations occur and passes that Se up the benthic food web".*

Tetra Tech Response: This means the presence of Corbula is an important part of the problem of selenium bioconcentration in the food chain, relative to other species of bivalves. Looking at recent bivalve data (after the June 19 version of TM-6 was prepared), we agree with the reviewer's comment that selenium concentrations in bivalves may be decreasing in recent years, although they show large inter-annual variations, and the model is predicting that change well. In the revised executive summary, the sentence referenced above has been modified as suggested.

Reviewer's Comment 4: *Doblin defines the Delta as "sites above Chipps Island". The most landward site was Rio Vista (I was on many of these cruises). These were all sites within the tidal influence of the Bay and therefore the particulate material there originates from the Bay and is strongly influenced by Se-contaminated Suisun Bay. Thus this boundary condition is not a riverine endmember but is river particulates mixed with Bay particulates, similar to the RMP "Sacramento River" site. In the end, in the model, Se concentrations on particulates were still kept constant and the boundary condition was derived from a Bay-influenced location samples by Doblin. The effect is to overestimate the Sacramento River boundary concentration and probably underestimate the SJR boundary compared to what is the reality. Pp. 2-43. Similarly the seawater boundary condition is a constant that is from a location strongly influenced by the Bay. This is more complex and probably less important to the TMDL, however. There is a great need for more data collection from the real river endmembers and from the coastal endmember.*

Tetra Tech Response: Without particulate selenium data from the real end member (Vernalis or Freeport), we can only use data from Delta as inputs to the Bay. We agree some of the Rio Vista particulate selenium data may reflect Bay influence or mixed with the San Joaquin River, but at least should be dominantly Sacramento River input during high flow (as estimated using DAYFLOW values and salinity measurements at the time of Se sampling). If we assume particulate selenium measured at Rio Vista during high flow reflects inputs from Sacramento River well, then the load from Sacramento River during high flow should be estimated reasonably well. We used the Delta data to derive Kd values for the SJR input. Although the SJR input may be underestimated, the Delta's effects of the SJR input need to be considered as well. After all, SJR enters the Bay through the Delta. We revised the text (p2-43) that particulate selenium from Rio Vista and Delta sampling stations may have bay influence.

Reviewer's Comment 5: *P3-32. The conclusions about predictions of dissolved Se should state something like: "the model captured the central tendencies of concentration of Se in the estuary as well as seasonal variations. But many of the highest peak concentrations were not well predicted, suggesting a cause that was outside of the conditions and/or assumptions set for the model." This is captured in a phrase on p. 3-37, but the longer explanation on p. 3-32 should be just as direct. Similarly, in Fig. 3-40 and 3-41, the model does a very good job of capturing the central tendency of the particulate Se data, but it does not capture some of the higher concentrations. Fig. 3-41 shows a better fit, but it should as it builds from two boundary conditions defined by the average Se on particulate material; nevertheless, the two highest data points are not predicted by the model in these transects. When Doblin et al sampled particulates at two stations through time there were a number of instances of concentrations elevated above the central tendency of the data. I think some point must be made of this weakness in the model, if it is to be used into the future. Indeed the conclusions on pg 3-55 is correct: "the model represents key features".. But a balanced report would follow that with a statement about the difficulty of predicting episodic increases in Se concentration. The model somehow does not capture their source. I think you could also add that "these features probably lie in the complexity of inputs from the rivers and interactions in the Delta that are poorly known." Personally, I think it is likely that there are times when more SJR water enters the Bay than the model assumes. For example, an under-prediction could result from higher Se in the SJR*

in the early years and a lower Delta capturing efficiency when the barriers are in or when the ratio of the two river discharges is at one extreme or the other. I do not know how one would incorporate that into a model…we just don't know enough. But it is important to be frank about, in case these periodic changes are biologically important.

Tetra Tech Response: We thank the reviewer for pointing out these caveats. We revised the discussion on P3-32 to say that some of the high concentrations are not captured by the model and this may be due to variations in load inputs that are not represented well by the model, and incorporated the discussion above.

With respect to the higher concentrations in Figure 3-40 and 3-41, some of these may also be due to in-situ processes of sediment suspension (PSe0) or variations in phytoplankton concentrations or species (POrgSe). This has also been added to the report.

Reviewer's Comment 6: *In describing Fig. 3-29, the model predicts an increasing concentration of Se in clams between the Carquinez Straits to the Golden Gate. There is only data from one station in San Pablo Bay but those data do not support this (and that is consistently the case in later data from that site). Otherwise the agreement is good. A more direct statement about the difference between prediction and observation would help, if only to emphasize that the San Pablo to the Golden Gate area might need more information. What was the outcome of the study you all did of Se in bivalves? Did such a geographic trend appear? Why isn't that data mentioned? Would be a good way to determine if this area that the model has trouble with or is just an anomaly resulting from the location of the USGS San Pablo Bay station.*

Tetra Tech Response: The trend appears to be evident that bivalve selenium concentrations increase from Carquinez Strait to San Pablo Bay (although there is only 1 station in San Pablo Bay). Data from Stewart (Stewart, R. 2007. Within Delta Conveyance: Environmental Water Quality Issues. CALFED Science Program Workshop Summary. Science Issues Relating to Delta Conveyance Infrastructure: Through Delta Options. September 11, 2007) showed an increasing trend of selenium concentrations towards higher salinity, although the data only extend to San Pablo Bay, not to Central Bay. This only indicates more data in the Central Bay are needed. As particulate selenium concentrations seem to increase toward central bay, there is no reason to reject the hypothesis that selenium concentrations in bivalves also increased towards that direction. The report is revised to note (on page 3-38) the limited data now used for the model comparison (temporal and spatial extent) and the need for comparisons with additional data.

The clam data collected by us are shown below (and compared to published data) (Figures 2 and 3). These were for a single point in time (late 2008) compared to other data used in the model evaluation from the 1990's. A comparison of the model with these data as well as others in the interim period (i.e., between 2000 and 2008) can be presented when such data become available.

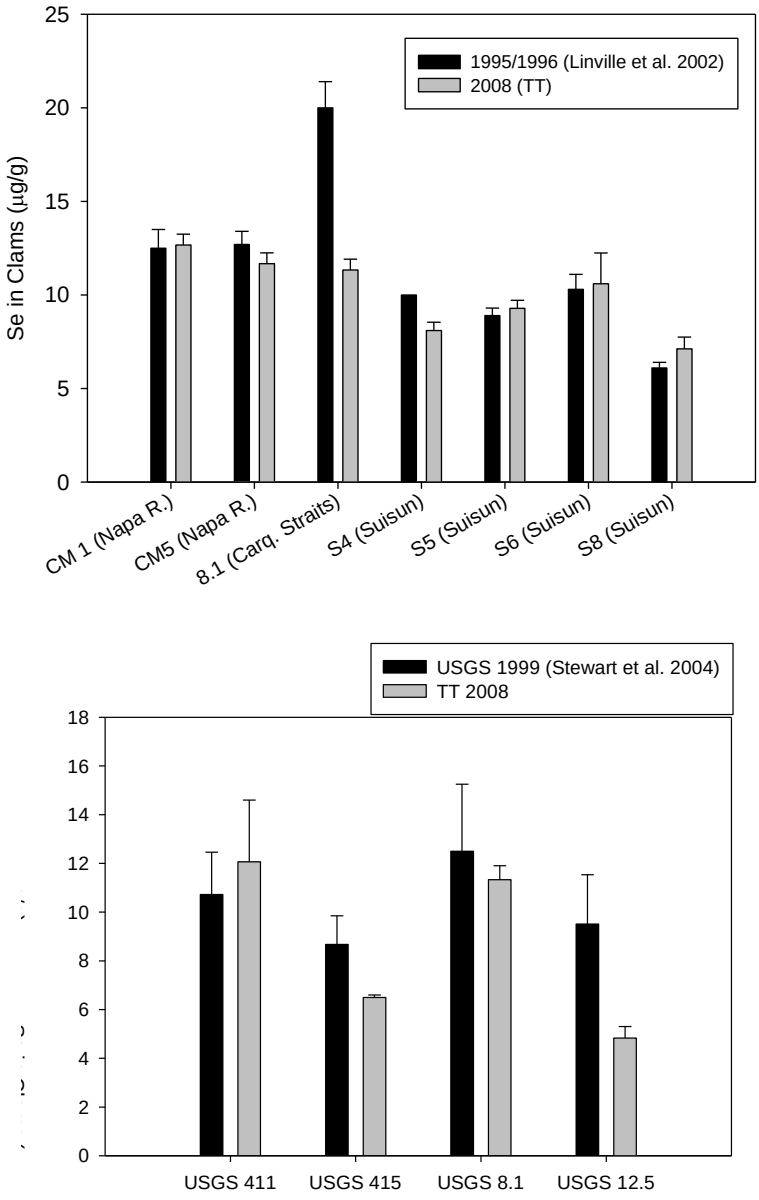

Figure A.5-2 November 2008 clam sampling by Tetra Tech, using sampling and analysis protocols identical to those of USGS, compared to published values.

Figure A.5-3 Map of November 2008 clam sampling by Tetra Tech, using sampling and analysis protocols identical to those of USGS.

Reviewer's Comment 7: *I was especially interested in the uptake rate/mineralization rate discussion and testing of this against field data. It was a nice discussion. The rate of Se uptake by phytoplankton was a source of some discussion by the review committee. On page 2-9 you make an insightful statement that I believe helps resolves this when you state both the rates and the concentrations at which those were determined. As the authors know, the rates estimated by Baines and by Reidel are rates, not rate constants. Rate of uptake is a function of Se concentration, of course; the contentious question being to what concentration does Se concentration accumulate in phytoplankton if Se in the water increases. The rate constant times the concentration gives the absolute rate at any concentration, assuming the relationship between the two can be defined mathematically (which, of course is a subject of some discussion if one looks at the shape of the Baines & Fisher M-M curve). But one could also estimate a rate constant for Se uptake by plotting the rates of uptake found by Baines' study and the one found by Reidel against the average concentration in those two studies (I know, only two data points). The slope is the rate constant of uptake (we call it K_u) in ug/g/d per ug/L or L/g/d. The rate constant is (2/0.3)/.02/10 = 0.013. Interestingly this is very similar (within the same order of magnitude) to the Ku (rate constant of uptake) by animals for selenite. That helps us address the discussion of how or if Se uptake by phytoplankton changes as concentration changes. The differences between the studies of Reidel and Baines is direct evidence that there is indeed a change in Se taken up over this concentration range, if one takes both studies as equally valid. In that case, how much Se bioaccumulation would be expected between Baines' range of concentrations? At a K_u of 0.013, a 10 fold increase in concentration would result in a (10X.013) thirteen percent increase in Se uptake. Not too different from what Steve and Nick suggest. Just a thought.*

Tetra Tech Response: This is a very good point, and an interesting point of discussion with the TRC. Does this argue against the use of a direct linear relationship between dissolved and phytoplankton concentrations?

Reviewer's General Comment: *Overall, I would say an excellent report, but it still has a few kinks that could unnecessarily ignite emotions. I very much respect the serious and thorough effort to address the quite knotty problems raised by the comments. By participating in the building of this model we all have learned a great deal about Se in the Bay that can be constructively applied to the TMDL. I believe there is much to recommend an ongoing use of this model as the TMDL is implemented and, hopefully, a monitoring program is implemented.*

A5.5 Conference Call with TRC to Discuss Comments and Responses, October 26, 2009.

A final conference call with the TRC members was conducted on October 26, 2009 to discuss the findings from the review process and to present a revised version of TM6 that incorporate the responses to the additional comments received from TRC (see Item 4 above). The following points, prepared by the Water Board, provide a summary of the understanding of the outcome of the discussions and recommendations derived from the TRC process.

- The model is a legitimate tool to use in evaluating scenarios and can be constructively applied to the TMDL development process.

- The technical memorandum reflects the current state of knowledge of biogeochemical transformations of selenium and processes leading to selenium bioaccumulation in the North Bay.

- All available data have been used in setting-up, testing, calibration and validation of the model.

- The scenarios evaluated in the model allow us to examine model performance. Additional scenarios can be evaluated using this model to support a linkage analysis and to examine the potential for recovery of the system given different scenarios.

- The revised report demonstrates that the model is robust, provides details of the underlying assumptions built into the model, and identifies potential limitations of the model and the available data.

The outcome of this final meeting with the TRC was a general consensus on these summary points. However, the TRC members requested clarification of two key points:

- The need to explicitly state the importance as well as the uncertainty associated with the values selected to represent the particulate selenium concentrations at the Sacramento River, which represents one of the boundary conditions.

- The need for a more focused data collection efforts and laboratory studies to better characterize the transformations between different forms of selenium.

In this document, the *Draft Final Technical Memorandum 6: Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay*, the Executive Summary and Section 6 (Discussion) were revised in response to the comments received from the TRC during this teleconference and subsequent e-mail exchanges to highlight both the importance and the uncertainties in riverine and ocean boundary conditions and their effect on the model results and the conclusions. It is noted in the revised document that future model development may seek to address some of the shortcomings of the modeling presented it this report, but such model development must be preceded by an adequate data collection program.

A5.6 APPENDIX REFERENCES

Tetra Tech, Inc. 2008. Technical Memorandum #8. Recommendations for the Technical Review Committee. April 2008. Report to the Regional Water Quality Control Board, San Francisco Bay Region.

RWQCB, 2007. Project Plan: North San Francisco Bay Selenium TMDL. July 2007.

APPENDIX 6: SUPPORTING CALCULATIONS FOR THE AUGUST 12, 2009 COMMENTS FROM REGINA LINVILLE (APPENDIX 5, PAGE A.5-26)

Table A.6-1
Example Calculation

Table 1: Example Calculation

Description	Value	Units	Source
Flow (avg Nov 1999)	3.4×10^{10}	l/d	DAYFLOW
PSP	0.010	g/l	Estimate
Elemental Se in PSP (Se OPSP)	0.1	ug/g	Table 3-3 of TM6
Selenite/Selenate in PSP (Se (IV + VI))	0.202	ug/g	Table 3-3 of TM6
Organic Se PSP (Org Se-II)	0.166	ug/g	Table 3-3 of TM6
Organic Se in Phyto	15.9	ug/g C	Table 3-2 of TM6
Chla	1.2	ug/L	(reflects delta at low flow 1999, see Fig 2 of Doblin)
C:Chla	51 mg C/ mg Chla	mg C	Table 3-2 of TM6
Phytoplankton	0.06	mg C/L	0.0012 mg Chla/L * 51 mg C/mg Chla
Loads			
Elemental Se in PSP (Se OPSP)	34	g Se/d	flow (l/d) * PSP (g/l) * Se OPSP PSP (ug/g) = ug Se/d
Selenite/Selenate in PSP (Se (IV + VI))	68	g Se/d	flow (l/d) * PSP (g/l) * Se (IV + VI) PSP (ug/g) = ug/d
Organic Se PSP (Org Se-II)	**56**	**g Se/d**	**flow (l/d) * PSP (g/l) * Org Se-II PSP (ug/g) = ug/d**
Total Se on PSP	159	g Se/d	Se OPSP PSP + Se (IV + VI) PSP + Org Se-II PSP g Se/d
Organic Se in Phyto	**33**	**g Se/d**	**flow (l/d) * C g/L * 15.9 ug Se/g C = ug/d**

Table A.6-2
Relative Sources of Selenium Assimilated into Bivalves Based on Low=flow Model Simulation in Figure 4-20*

Table 2: Relative sources of selenium assimilated into bivalves based on low-flow model simulations in Figure 4-20 ‡ §

	Bioavailable Particulate Se				Bioavailable Particulate Organic Se			Bioavailable Se by Model Compartment		
		% of all Bio P Se				% of Bio P Se (-II)		% of all Bio P Se		
Salinity	Total Particulate Bioavailable Se (Bio P Se)	Sedi‡‡	Detritus	Phyto	Organic Particulate Bioavailable Se (Bio P Se (-II))	PSP	Phyto	PSP	BESP	Phyto
	ug/g	%	%	%	ug/g	%	%	%	%	%
0	0.139	46%	25%	29%	0.075	46%	54%	45%	26%	29%
2.5	0.128	46%	22%	31%	0.069	42%	58%	41%	28%	31%
5	0.163	36%	25%	39%	0.104	39%	61%	45%	16%	39%
10	0.284	29%	26%	45%	0.203	37%	63%	48%	7%	45%
15	0.392	26%	29%	45%	0.288	39%	61%	52%	3%	45%
20	0.516	24%	28%	48%	0.392	37%	63%	51%	1%	48%
25	0.662	23%	28%	48%	0.507	37%	63%	51%	0%	48%
30	0.755	25%	31%	45%	0.566	41%	59%	55%	0%	45%

‡ Using parameters for Se speciation in PSP and assimilation efficiency factors from the model (AE = 0.2, 0.45 and 0.8 for elemental Se, Se IV/VI, and organic Se, see tables 4 & 5).

§ Estimations of organic Se in PSP are likely artificially elevated at higher salinities since selenite is added to PSP as it travels through the estuary.

‡‡ Sediment is all inorganic selenium (from PSP and BESP)

Table A.6-3
Realative Sources of Selenium Assimilated into Bivalves on Simulation for Carquinez Strait in Figure 4-21*

Table 3: Relative sources of selenium assimilated into bivalves based on simulations for Carquinez Strait in Figure 4-21 ‡

	Bioavailable Particulate Se				Bioavailable Particulate Organic Se			Bioavailable Se by Model Compartment		
		% of all Bio P Se				% of Bio P Se (-II)		% of all Bio P Se		
Date	Total Particulate Bioavailable Se (Bio P Se)	Sedi‡‡	Detritus	Phyto	Organic Particulate Bioavailable Se (Bio P Se (-II))	PSP	Phyto	PSP	BESP	Phyto
	ug/g	%	%	%	ug/g	%	%	%	%	%
Jun-98	0.222	36%	39%	25%	0.142	61%	39%	71%	4%	25%
Nov-98	0.242	35%	38%	26%	0.156	59%	41%	69%	4%	26%
Mar-99	0.159	45%	45%	10%	0.088	82%	18%	82%	8%	10%
Nov-99	0.448	25%	28%	46%	0.335	38%	62%	51%	2%	46%

‡ Using parameters for Se speciation in PSP and assimilation efficiency factors from the model (AE = 0.2, 0.45 and 0.8 for elemental Se, Se IV/VI, and organic Se, see tables 4 & 5).

‡‡ Sediment is all inorganic selenium (from PSP and BESP)

Table A.6-4
Interpreted Data from Figure 4-20 and 4-21 in TM6

Table 4: Interpreted Data from Fig 4-20 & 4-21 in TM6

Data interpreted from Fig 4-20. Nov 1999 Particulate selenium through estuary

	PSP*				BESP	Phyto
	Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
Salinity	ug/g				ug/g	ug/g
0	0.12	0.025	0.052	0.043	0.18	0.05
2.5	0.10	0.021	0.043	0.036	0.18	0.05
5	0.14	0.029	0.060	0.050	0.13	0.08
10	0.26	0.055	0.112	0.094	0.10	0.16
15	0.39	0.082	0.168	0.140	0.06	0.22
20	0.50	0.105	0.215	0.180	0.03	0.31
25	0.65	0.137	0.280	0.234	0.01	0.40
30	0.80	0.168	0.344	0.288	0.00	0.42

PSP*				BESP	Phyto
Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
ug/L				ug/L	ug/L
0.0045	0.0009	0.0019	0.0016	0.007	0.0019
0.0044	0.0009	0.0019	0.0016	0.0078	0.0021
0.0042	0.0009	0.0018	0.0015	0.005	0.0022
0.0043	0.0009	0.0018	0.0015	0.0018	0.0024
0.0043	0.0009	0.0018	0.0015	0.0008	0.0026
0.0043	0.0009	0.0018	0.0015	0.0002	0.0027
0.0045	0.0009	0.0019	0.0016	0.0001	0.0026
0.0046	0.0010	0.0020	0.0017	0	0.0025

Data interpreted from Fig 4-21. Particulate selenium at Carquinez Strait

	PSP*				BESP	Phyto
	Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
Date	ug/g				ug/g	ug/g
Jun-98	0.3	0.063	0.129	0.108	0.045	0.07
Nov-98	0.32	0.067	0.138	0.115	0.05	0.08
Mar-99	0.25	0.053	0.108	0.090	0.06	0.02
Nov-99	0.44	0.092	0.189	0.158	0.05	0.26

PSP*				BESP	Phyto
Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
ug/L				ug/L	ug/L
0.0170	0.0036	0.0073	0.0061	0.0015	0.0030
0.0065	0.0014	0.0028	0.0023	0.0015	0.0040
0.0220	0.0046	0.0095	0.0079	0.0090	0.0020
0.0045	0.0009	0.0019	0.0016	0.0008	0.0025

*** PSP speciation estimated from paramters in Table 3-3 of TM6 (as percentages of total Se in PSP)**

Se Species in PSP	ug/g	% of Total PSP Se
Elemental	0.1	21%
Selenite/ selenate	0.202	43%
Organic	0.166	36%
Total Se	0.468	

Table A.6-5
Calculations of Bioavailabilty Se from Figures 4-20 and 4-21 in TM6

Table 5: Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/g
(Particulate Se simulated for low-flow)

		Bioavailable Se by Model Compartment						Bioavailable Se by Partical Type					
	Total Particulate Bioavail Se (Bio P Se)	PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
		Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
Salinity	ug/g	ug/g	%	ug/g	%	ug/g	%	ug/g	%	ug/g	%	ug/g	%
0	0.139	0.063	45%	0.036	26%	0.040	29%	0.064	46%	0.035	25%	0.040	29%
2.5	0.128	0.052	41%	0.036	28%	0.040	31%	0.060	46%	0.029	22%	0.040	31%
5	0.163	0.073	45%	0.026	16%	0.064	39%	0.059	36%	0.040	25%	0.064	39%
10	0.284	0.136	48%	0.020	7%	0.128	45%	0.081	29%	0.075	26%	0.128	45%
15	0.392	0.204	52%	0.012	3%	0.176	45%	0.104	26%	0.112	29%	0.176	45%
20	0.516	0.262	51%	0.006	1%	0.248	48%	0.124	24%	0.144	28%	0.248	48%
25	0.662	0.340	51%	0.002	0%	0.320	48%	0.155	23%	0.187	28%	0.320	48%
30	0.755	0.419	55%	0.000	0%	0.336	45%	0.188	25%	0.230	31%	0.336	45%

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/L
(Particulate Se simulated for low-flow)

		Bioavailable Se by Model Compartment						Bioavailable Se by Partical Type					
	Total Particulate Bioavail Se (Bio P Se)	PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
		Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
Salinity	ug/l	ug/l	%	ug/l	%	ug/l	%	ug/l	%	ug/l	%	ug/l	%
0	0.0053	0.002	45%	0.001	27%	0.00152	29%	0.002	47%	0.0013	25%	0.0015	29%
2.5	0.0055	0.002	42%	0.002	28%	0.00168	30%	0.003	47%	0.0013	23%	0.0017	30%
5	0.0050	0.002	44%	0.001	20%	0.00176	35%	0.002	40%	0.0012	24%	0.0018	35%
10	0.0045	0.002	50%	0.000	8%	0.00192	42%	0.001	30%	0.0012	27%	0.0019	42%
15	0.0045	0.002	50%	0.000	4%	0.00208	46%	0.001	26%	0.0012	28%	0.0021	46%
20	0.0045	0.002	51%	0.000	1%	0.00216	49%	0.001	24%	0.0012	28%	0.0022	49%
25	0.0045	0.002	53%	0.000	0%	0.00208	47%	0.001	24%	0.0013	29%	0.0021	47%
30	0.0044	0.002	55%	0.000	0%	0.00200	45%	0.001	25%	0.0013	30%	0.0020	45%

Table A.6-5 (continued)
Calculations of Bioavailabilty Se from Figures 4-20 and 4-21 in TM6

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/g
(Particulate Se simulated at Carquinez Straight)

		Bioavailable Se by Model Compartment						Bioavailable Se by Partical Type					
	Total Particulate Bioavail Se (Bio P Se)	PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
		Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
Date	**ug/g**	**ug/g**	**%**	**ug/g**	**%**	**ug/g**	**%**	**ug/g**	**%**	**ug/g**	**%**	**ug/g**	**%**
Jun-98	**0.222**	0.157	**71%**	0.009	**4%**	0.056	**25%**	0.080	**36%**	0.086	**39%**	0.056	**25%**
Nov-98	**0.242**	0.168	**69%**	0.010	**4%**	0.064	**26%**	0.085	**35%**	0.092	**38%**	0.064	**26%**
Mar-99	**0.159**	0.131	**82%**	0.012	**8%**	0.016	**10%**	0.071	**45%**	0.072	**45%**	0.016	**10%**
Nov-99	**0.448**	0.230	**51%**	0.010	**2%**	0.208	**46%**	0.114	**25%**	0.127	**28%**	0.208	**46%**

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/L
(Particulate Se simulated at Carquinez Straight)

		Bioavailable Se by Model Compartment						Bioavailable Se by Partical Type					
	Total Particulate Bioavail Se (Bio P Se)	PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
		Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
Date	**ug/l**	**ug/l**	**%**	**ug/l**	**%**	**ug/l**	**%**	**ug/l**	**%**	**ug/l**	**%**	**ug/l**	**%**
Jun-98	**0.0116**	0.009	**77%**	0.000	**3%**	0.00240	**21%**	0.004	**37%**	0.0049	**42%**	0.0024	**21%**
Nov-98	**0.0069**	0.003	**49%**	0.000	**4%**	0.00320	**46%**	0.002	**27%**	0.0019	**27%**	0.0032	**46%**
Mar-99	**0.0149**	0.012	**77%**	0.002	**12%**	0.00160	**11%**	0.007	**47%**	0.0063	**42%**	0.0016	**11%**
Nov-99	**0.0045**	0.002	**52%**	0.000	**4%**	0.00200	**44%**	0.001	**27%**	0.0013	**29%**	0.0020	**44%**

Table A.6-5 (continued)
Calculations of Bioavailabilty Se from Figures 4-20 and 4-21 in TM6

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/g
(Particulate Se simulated for low-flow)

		Bioavailable Se from PSP							Bioavailable Particulate Organic Se				
		PSP							Particulate Organic Se				
	Total Particulate Bioavail Se (Bio P Se)	Total	Elemental		Selenite / Selenate		Org Se		All Particulate Organic Se (Bio Org Se)	PSP Org Se		Phyto Org Se	
		Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP		Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se
Salinity	ug/g	ug/g	ug/g	%	ug/g	%	ug/g	%	ug/g	ug/g	%	ug/g	%
0	0.139	0.063	0.005	8%	0.023	37%	0.035	55%	0.075	0.035	46%	0.040	54%
2.5	0.128	0.052	0.004	8%	0.019	37%	0.029	55%	0.069	0.029	42%	0.040	58%
5	0.163	0.073	0.006	8%	0.027	37%	0.040	55%	0.104	0.040	39%	0.064	61%
10	0.284	0.136	0.011	8%	0.050	37%	0.075	55%	0.203	0.075	37%	0.128	63%
15	0.392	0.204	0.016	8%	0.075	37%	0.112	55%	0.288	0.112	39%	0.176	61%
20	0.516	0.262	0.021	8%	0.097	37%	0.144	55%	0.392	0.144	37%	0.248	63%
25	0.662	0.340	0.027	8%	0.126	37%	0.187	55%	0.507	0.187	37%	0.320	63%
30	0.755	0.419	0.034	8%	0.155	37%	0.230	55%	0.566	0.230	41%	0.336	59%

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/L
(Particulate Se simulated for low-flow)

		Bioavailable Se from PSP							Bioavailable Particulate Organic Se				
		PSP							Particulate Organic Se				
	Total Particulate Bioavail Se (Bio P Se)	Total	Elemental		Selenite / Selenate		Org Se		All Particulate Organic Se (Bio Org Se)	PSP Org Se		Phyto Org Se	
		Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP		Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se
Salinity	ug/l	ug/l	ug/l	%	ug/l	%	ug/l	%	ug/l	ug/l	%	ug/l	%
0	0.0053	0.002	0.00019	8%	0.00087	37%	0.00130	55%	0.00282	0.00130	46%	0.00152	54%
2.5	0.0055	0.002	0.00018	8%	0.00085	37%	0.00127	55%	0.00295	0.00127	43%	0.00168	57%
5	0.0050	0.002	0.00018	8%	0.00081	37%	0.00121	55%	0.00297	0.00121	41%	0.00176	59%
10	0.0045	0.002	0.00018	8%	0.00083	37%	0.00124	55%	0.00316	0.00124	39%	0.00192	61%
15	0.0045	0.002	0.00018	8%	0.00083	37%	0.00124	55%	0.00332	0.00124	37%	0.00208	63%
20	0.0045	0.002	0.00018	8%	0.00083	37%	0.00124	55%	0.00340	0.00124	36%	0.00216	64%
25	0.0045	0.002	0.00019	8%	0.00087	37%	0.00130	55%	0.00338	0.00130	38%	0.00208	62%
30	0.0044	0.002	0.00019	8%	0.00089	37%	0.00132	55%	0.00332	0.00132	40%	0.00200	60%

Table A.6-5 (continued)
Calculations of Bioavailabilty Se from Figures 4-20 and 4-21 in TM6

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/g
(Particulate Se simulated at Carquinez Straight)

		Bioavailable Se from PSP							Bioavailable Particulate Organic Se				
		PSP							Particulate Organic Se				
		Total	Elemental		Selenite / Selenate		Org Se			PSP Org Se		Phyto Org Se	
	Total Particulate Bioavail Se (Bio P Se)	Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	All Particulate Organic Se (Bio Org Se)	Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se
Date	ug/g	ug/g	ug/g	%	ug/g	%	ug/g	%	ug/g	ug/g	%	ug/g	%
Jun-98	0.222	0.157	0.013	8%	0.058	37%	0.086	55%	0.142	0.086	61%	0.056	39%
Nov-98	0.242	0.168	0.013	8%	0.062	37%	0.092	55%	0.156	0.092	59%	0.064	41%
Mar-99	0.159	0.131	0.011	8%	0.048	37%	0.072	55%	0.088	0.072	82%	0.016	18%
Nov-99	0.448	0.230	0.018	8%	0.085	37%	0.127	55%	0.335	0.127	38%	0.208	62%

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
(Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/L
(Particulate Se simulated at Carquinez Straight)

		Bioavailable Se from PSP							Bioavailable Particulate Organic Se				
		PSP							Particulate Organic Se				
		Total	Elemental		Selenite / Selenate		Org Se			PSP Org Se		Phyto Org Se	
	Total Particulate Bioavail Se (Bio P Se)	Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	All Particulate Organic Se (Bio Org Se)	Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se
Date	ug/l	ug/l	ug/l	%	ug/l	%	ug/l	%	ug/l	ug/l	%	ug/l	%
Jun-98	0.0116	0.009	0.00071	8%	0.00329	37%	0.00490	55%	0.00730	0.00490	67%	0.00240	33%
Nov-98	0.0069	0.003	0.00027	8%	0.00126	37%	0.00187	55%	0.00507	0.00187	37%	0.00320	63%
Mar-99	0.0149	0.012	0.00092	8%	0.00426	37%	0.00634	55%	0.00794	0.00634	80%	0.00160	20%
Nov-99	0.0045	0.002	0.00019	8%	0.00087	37%	0.00130	55%	0.00330	0.00130	39%	0.00200	61%